Monitoring Polycyclic Aromatic Hydrocarbon Concentrations in Austin, TX, After the Coal-Tar Sealant Ban

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Abstract

Polycyclic Aromatic Hydrocarbons (PAH) are a group of chemicals consisting of three or more fused benzene rings. Many of this group of compounds are considered Toxic Pollutants and listed as Priority Pollutants by the EPA. In 2006, the City of Austin enacted a ban on coal-tar sealant to remove a source of PAH contamination to Austin creeks. Sediment samples collected in approximately 50 of Austin's largest watersheds from 1996 until 2010 were analyzed. The total PAH concentration of these samples was calculated as the sum of the 16 compounds found within the first EPA Priority Pollutant list. Kruskal-Wallis analysis and regression analysis were used to determine any temporal trends in Austin as a whole and at individual sites. 3-ringed PAH were significantly higher in 1996-1999 compared to 2003-2005, 2006-2008, and 2009-2010; and 4-ringed PAH were significantly higher in 1996-1999 compared to 2006-2008. Total PAH significantly decreased at Barton Creek above Barton Springs Pool from 1996 to 2010. While PAH concentrations at the majority of Austin locations were less than the Probable Effect Concentration (above which adverse effects on aquatic organisms are expected to occur), there were several sites where PAH concentrations were above urban background levels found in the literature. These sites require additional investigation to isolate and potentially remediate sources of PAH.

Introduction

Polycyclic Aromatic Hydrocarbons (PAH) are a group of chemical compounds consisting of three or more fused benzene rings. The number of rings and the shape of the ring structure both play a role in the chemical properties of the different PAH. These compounds are currently on the Toxic Pollutants and Priority Pollutants lists of the Code of Federal Regulations at 40 CFR 401.15 and 40 CFR 423 Appendix A, respectively. PAH are considered Toxic Pollutants because they persist in the environment; several are toxic, carcinogenic, mutagenic, and/or teratogenic (causing birth defects) to aquatic life; and seven are probable human carcinogens (U.S. Environmental Protection Agency, 2012).

PAH are able to persist in the environment because they generally have a high affinity to sediment, low volatility, and a high resistance to biodegradation (McElroy *et al* 1989). These compounds are hydrophobic and tend to sorb to particulates in the water column, eventually settling to the substrate of water bodies as sediment. Concentrations in the sediment tend to be much higher than concentrations in the water column due to the low solubility of PAH (Moore and Ramamoorthy 1984). The solubility decreases as molecular weight increases, so PAH with 4 or more rings (heavier) are more likely to sorb to sediments more than the PAH with 2 or 3 rings. PAH with 2 or 3 rings can readily volatilize (convert from liquid to solid state) while PAH with 4 or more rings show limited volatilization under many environmental conditions (Moore and Ramamoorthy 1984). The main source of decomposition of PAH in sediments is microbial degradation (Cerniglia 1992). Lower molecular weight PAH can be degraded readily under aerobic and anaerobic conditions while higher molecular weight PAH are more resistant (Mrozik *et al* 2003, Leduc *et al* 1992, Cerniglia 1992). While higher molecular weight PAH are more resistant, there do exist bacteria known to degrade them although at slower rates than the lower molecular weight PAH (Krivobok *et al* 2003). It has also been shown that PAH introduced into a pristine system may not be degraded at first; however, microorganism communities can develop over time in a polluted site that can degrade both high and low molecular weight PAH (Coates *et al* 1997). Thus, if sources of PAH contamination can be eliminated the concentration of PAH can return to a background level given enough time.

PAH are formed whenever carbon-based compounds experience incomplete combustion. This can occur naturally via volcanic activity and forest fires, so even in pristine environments there will be some background level of PAH present. However, these sources are not thought to be significant contributions of modern PAH input to the environment (Sims and Overcash 1983, Wild and Jones 1995). Major anthropogenic sources include the combustion of materials to make energy and the combustion in waste incineration (Ramdahl *et al* 1983, Wild and Jones 1995). Problems tend to occur in urban environments where the concentrations of PAH are higher due to the increased number of sources and continuous loading. Sources such as carbon production, petroleum processing, residential heating, power plant generation, and gasoline engines of cars are included as anthropogenic sources for PAH creation. With a plethora of sources in an urban area it is common to find a higher background level of PAH presence in the urban environment (Stout *et al* 2004).

Due to the abundance of compounds classified as PAH and the fact that these compounds are typically found in groups, there exist over 100 known combinations of PAH. The most common grouping that is evaluated for regulatory purposes is the combination of 15 PAH (acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, ideno(1,2,3-cd)pyrene, phenanthrene, and pyrene) with one bicyclic aromatic hydrocarbon (naphthalene). These 16 compounds made up the original list of EPA Priority Pollutant PAH. Sediments with a total concentration above 20,000 µg/Kg of the EPA 16 Priority Pollutant PAH are considered to occur at a level above urban background (Stout *et al* 2004). In addition, harmful effects are expected to occur on bottom-dwelling biota when sediments contain 22.8 mg/Kg PAH, the Probable Effect Concentration although toxic effects for individual PAH components are as low as 1.6 mg/Kg (MacDonald *et al* 2000).

Research conducted by the US Geological Survey (USGS) has identified coal-tar based pavement sealant as another significant anthropogenic source of PAH (Mahler *et al* 2005, Mahler and Van Metre 2011). Pavement sealant is a coal-tar or asphalt based black liquid sprayed on asphalt pavements, primarily parking lots. Once dry, the sealant binds to the surface layer and slows wear and degradation of the asphalt to prolong its useful life. Coal-tar-based sealants contain about 20 to 35 percent coal-tar pitch which is 50% or more PAH by weight and a known human carcinogen (Mahler and Van Metre 2011, US Department of Human Health Services 2011). During a 2007-08 study by USGS, dust collected from parking lots sealed with a coal-tar-based sealant had a median PAH concentration of 2,200 mg/Kg while dust collected from parking lots that used an asphalt based sealant had a median PAH concentration of 2.1 mg/Kg (Mahler and Van Metre 2011). In a related study, the USGS collected sediment cores in 40 US lakes in order to determine sources of PAH in the sediment. Using the chemical "fingerprint" of PAH the USGS was able to show that coal-tar-based sealant accounted for half of all PAH in the lake (Van Metre and Mahler 2010). Concentrations in lakes contaminated by PAH from coal-tar sealant were higher than the Probable Effect Concentration (PEC) while concentrations of PAH from other sources were not above this level.

The City of Austin, in cooperation with the US Geological Survey, conducted several studies from 2000 to 2005 that examined concentrations and sources of PAH in creeks and lakes in Austin, Texas (Great Lakes Environmental Center 2005, Mahler et al 2005, Geismar 2000). The City found that not only was coal-tar sealant from parking lot run-off a source of contamination to the Austin waterways, but the PAH levels in some of the creeks were detrimental to aquatic life (Bryer et al 2006, Great Lakes Environmental Center 2005). Based on this information the City of Austin enacted a ban on coal-tar based pavement sealant in 2006. This report examines PAH levels throughout Austin using data collected 5 years after the coal-tar based pavement sealant ban implemented in 2006.

Methods

The City of Austin has collected sediment samples near the mouths of creeks since 1996 as a component of the Environmental Integrity Index project (EII - Sediment). Sampling of different watersheds was rotated every three years from 1996 to 2008 so that one sediment sample was collected for each Austin watershed every three years. In 2009, due to an increase in the number of watersheds and sites per year, EII sediment sampling frequency increased to a two year cycle. One sample was collected from all monitored Austin watersheds from 2009 to 2010. Samples were collected between May and August and placed in glass jars before they were taken to DHL Laboratories, a NELAP approved laboratory, for analysis. Parameters of interest to this report that were analyzed include acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(ghi)perylene, benzo(a)pyrene, chrysene, dibenz(ah)anthracene, fluoranthene, fluorine, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, pyrene, and benzo(b)fluoranthene. The total PAH of a sample was calculated as the sum of these parameters. If a parameter was below the detectable limit of the analysis it was excluded from the summation, unless all parameters were below a detection limit. If every parameter was below the detection limit then the total PAH was calculated as the sum of all parameters but marked with a '<' symbol to designate that the PAH level was some value below the summation of detection limits.

In 2005, the City of Austin began a project to monitor additional sites for PAH in sediment called the PAH Specific Monitoring project. Samples were collected and analyzed similar to sediment samples collected for EII. The calculation for total PAH in a sample was also the same as EII samples. An entire site list with the project for which that site was sampled is shown in Table 1.

In order to investigate how total PAH in sediment throughout Austin has been changing since 1996, EII samples were grouped by the round collected and displayed in a box plot. A round consisted of the set of years in which all sample sites were collected once. The first round consisted of samples collected from 1996-1999, the second round lasted from 2000-2002, the third round from 2003-2005, the fourth round from 2006-2008, and round five lasted from 2009-2010. Samples between groups were compared statistically using the Kruskal-Wallis test to check for difference in overall PAH level (Hollander and Wolfe 1999). The minimum p-value method was used as a multiple comparison test when there was found to be some significant difference between rounds using the Kruskal-Wallis test (Richter and Higgins 2006). Similar analysis was done on individual PAH parameters and PAH grouped by ring number to determine which PAH were prevalent in Austin stream beds. Additionally, total PAH at each site was displayed in scatter plots to visualize temporal variation at different locations around Austin, Texas. Regression analysis was performed for total PAH at each site to statistically track any temporal change (Kutner *et al* 2005). Detection limits in earlier portions of the sampling period were higher than most detected values. Thus values below the detection limit were not used in any analysis. SAS 9.2 was used in all analysis with alpha levels set at 0.05 unless otherwise noted in the results.

Table 1: Site name, watershed, and project for sediment samples collected.

SITE	WATERSHED	PROJECT
Barton Creek Between Dams Upstream of Pool	Barton Creek	EII/PAH Monitoring
Barton Creek Upstream of Barton Spring Pool	Barton Creek	EII - Sediment
Bear Creek @ Twin Creeks Road	Bear Creek	EII - Sediment
Bear Creek (West) @ Fritz Hughes Park Road	Bear Creek West	EII - Sediment
Bee Creek @ Lake Austin	Bee Creek	EII - Sediment
Blunn Creek @ Riverside Drive	Blunn Creek	EII - Sediment
North Boggy Creek @ Delwau Lane	Boggy Creek	EII - Sediment
Bull Creek @ Loop 360 First Crossing	Bull Creek	EII/PAH Monitoring
Bull Creek Downstream of West Bull Creek	Bull Creek	EII - Sediment
Bull Creek Upstream of West Bull Creek	Bull Creek	EII - Sediment
Buttermilk Creek @ Little Walnut Creek	Buttermilk Branch	EII - Sediment
Buttermilk Creek @ Providence	Buttermilk Branch	EII - Sediment
Carson Creek @ Shady Spring Subdivision	Carson Creek	EII - Sediment
Carson Creek @ US 183	Carson Creek	PAH Monitoring
Common Ford Tributary in Common Ford Metro Park	Commons Ford Creek	EII - Sediment
Cottonmouth Creek @ Colton Road	Cottonmouth Creek	EII - Sediment
Cottonmouth Creek @ Dee Gabriel Collins Rd	Cottonmouth Creek	EII - Sediment

Table 1: Site name, watershed, and project for sediment samples collected (continued).

East Country Club @ ACC	Country Club East	EII - Sediment
East Country Club Creek Downstream of Grove Drive	Country Club East	EII - Sediment
West Country Club @ Krieg Field	Country Club West	EII - Sediment
Cuernavaca Creek @ River Hills Road	Cuernavaca Creek	EII - Sediment
Decker Creek @ FM 969	Decker Creek	EII - Sediment
Decker Creek @ Gilbert Rd	Decker Creek	EII - Sediment
Dry Creek @ FM 812	Dry Creek	EII - Sediment
Dry Creek @ River Road	Dry Creek	EII - Sediment
Dry Creek @ Wolf Lane	Dry Creek	EII - Sediment
Dry Creek (North) @ Highland Pass	Dry Creek North	PAH Monitoring
Dry Creek (North) @ Mt Bonnel Rd	Dry Creek North	EII - Sediment
Eanes Creek @ Rollingwood	Eanes Creek	EII - Sediment
East Bouldin Creek @ Elizabeth St	East Bouldin Creek	PAH Monitoring
East Bouldin Creek @ Post Oak	East Bouldin Creek	EII/PAH Monitoring
East Bouldin Creek @ Riverside Dr	East Bouldin Creek	EII - Sediment
East Bouldin Creek Downstream of W. Alpine Rd	East Bouldin Creek	PAH Monitoring
Elm Creek @ Austins Colony	Elm Creek	EII - Sediment
Elm Creek @ Milo Road	Elm Creek	EII - Sediment
Fort Branch Creek @ North Boggy Creek	Fort Branch	EII - Sediment
Fort Branch Creek @ Single Shot Circle	Fort Branch	PAH Monitoring
Gilleland Creek @ FM 969	Gilleland Creek	EII - Sediment
Harpers Branch Creek @ Riverside Dr	Harper's Branch	EII - Sediment
Harpers Branch Creek @ Woodland Ave	Harper's Branch	EII/PAH Monitoring
Harris Branch Creek @ Boyce Lane	Harris Branch	EII - Sediment
Harris Branch Creek @ Cameron Road	Harris Branch	EII - Sediment
Johnson Creek @ Stephen F Austin Drive	Johnson Creek	EII - Sediment
Johnson Creek @ Woodmont Avenue	Johnson Creek	EII - Sediment
Lady Bird Lake @ Basin (AC)	Lady Bird Lake	Town Lake Study
Lake Creek @ Sugar Berry Cove	Lake Creek	EII - Sediment
Little Barton Creek @ Barton Creek (LBC)	Little Barton Creek	EII - Sediment
Little Barton Creek @ Great Divide Dr	Little Barton Creek	PAH Monitoring
Little Barton Creek @ Hamilton Pool Rd	Little Barton Creek	PAH Monitoring
Little Bear Creek @ Bear Creek	Little Bear Creek	EII - Sediment
Little Bee Creek @ Red Bud Trail	Little Bee Creek	EII - Sediment
Little Walnut @ Cameron Rd	Little Walnut Creek	PAH Monitoring
Little Walnut Creek @ Golden Meadow Rd	Little Walnut Creek	PAH Monitoring
Little Walnut Creek @ US183	Little Walnut Creek	EII - Sediment
Marble Creek Upstream Onion Creek (M1)	Marble Creek	EII - Sediment
North Fork Dry Creek @ FM812	North Fork Dry Creek	EII - Sediment
Onion Creek @ FM 973	Onion Creek	EII - Sediment
Onion Creek @ South Austin Regional WWTP (SAR)	Onion Creek	EII - Sediment
Panther Hollow Creek @ Big View Road	Panther Hollow	EII - Sediment
Rattan Creek @ Shadowbrook Circle	Rattan Creek	EII - Sediment
Rinard Creek @ Bradshaw Road	Rinard Creek	EII - Sediment
Deer @ Running Deer Trail (AST)	Running Deer Creek	EII - Sediment
Shoal Creek @ West Avenue	Shoal Creek	EII - Sediment
Shoal Creek Upstream of 1st St.	Shoal Creek	EII - Sediment

Table 1: Site name, watershed, and project for sediment samples collected (continued).

Slaughter Creek @ IH35	Slaughter Creek	EII - Sediment
Slaughter Creek @ Pine Valley Drive	Slaughter Creek	EII - Sediment
South Boggy @ Congress Ave	South Boggy Creek	PAH Monitoring
South Boggy Creek @ Bluff Springs Road (BO1)	South Boggy Creek	EII - Sediment
South Boggy Creek @ W. Dittmar Rd	South Boggy Creek	PAH Monitoring
South Fork Dry Creek @ FM812	South Fork Dry Creek	EII - Sediment
Tannehill Creek @ Desirable Drive	Tannehill Branch	EII - Sediment
Tannehill Creek Upstream of Boggy Creek	Tannehill Branch	EII - Sediment
Taylor Slough North @ Mayfield Park	Taylor Slough North	EII - Sediment
Taylor Slough North @ Pecos St (TSN)	Taylor Slough North	EII/PAH Monitoring
Taylor Slough South Downstream of Reed Park	Taylor Slough South	EII - Sediment
Taylor Slough South @ Reed Park	Taylor Slough South	EII - Sediment
Taylor Slough South @ Scenic Drive	Taylor Slough South	EII - Sediment
Turkey Creek @ City Park Road	Turkey Creek	EII - Sediment
Waller Creek @ Pipe Upstream of 24th Street	Waller Creek	PAH Monitoring
Waller Creek Downstream of Cesar Chavez	Waller Creek	EII - Sediment
Walnut Creek @ Loyola Lane	Walnut Creek	PAH Monitoring
Walnut Creek @ SPRR Bridge	Walnut Creek	EII - Sediment
Walnut Creek Downstream of Metric Blvd	Walnut Creek	PAH Monitoring
Walnut Creek Upstream of Freescale	Walnut Creek	EII - Sediment
Lake Long @ Dam (LWL3)	Walter E. Long Lake	Lake Long Study
West Bouldin @ Cardinal	West Bouldin Creek	EII/PAH Monitoring
West Bouldin @ Post Oak	West Bouldin Creek	EII – Sediment
West Bouldin Creek @ Guerrero Park	West Bouldin Creek	PAH Monitoring
West Bouldin Creek @ Jewell	West Bouldin Creek	EII - Sediment
West Bull Creek Upstream of Bull Creek (EK)	West Bull Creek	EII – Sediment
Williamson Creek @ Hwy 71 (EII)	Williamson Creek	PAH Monitoring
Williamson Creek @ McKinney Falls (Will1)	Williamson Creek	EII - Sediment

Results

Kruskal-Wallis analysis showed some significant difference in total PAH between rounds at EII sites (p=0.0054); however, the minimum p-value analysis of EII sites did not show that total PAH was significantly different between any group of years. This suggests that the range of PAH concentrations between year groups overlaps enough to determine that there is no significant difference in total PAH between years. The box plot of total PAH collected at EII sites showed that a majority of PAH concentrations were lower in 2006-2008 and 2009-2010 (indicated by the lower medians) than in other years (Figure 1). However, there were still high concentrations of total PAH in these years, which raised the mean concentration of total PAH and reinforced the results of the minimum p-value analysis.

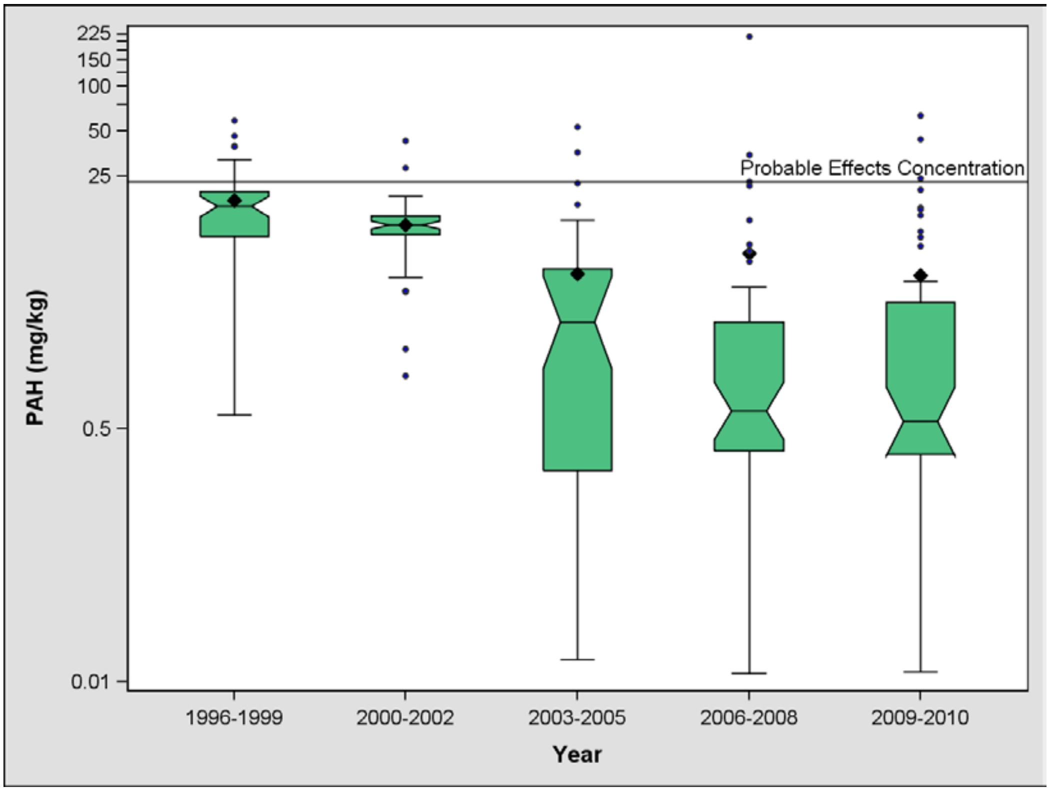

Figure 1: Box plot of total PAH (mg/Kg) collected in EII sampling from 1996-2010. Black diamonds◆represent means, notched lines ⧗ represent medians, and small circles • represent outliers.

PAH with only two rings were not detected in all annual groupings and were never above 0.02 mg/Kg when detected, so these data were not analyzed for significant differences. Analysis showed a significant difference in total 3-ringed PAH concentration between 1996-1999 and 2003-2005 ($p=0.0439$), 2006-2008 ($p=0.0264$), and 2009-2010 ($p=0.0303$) (Figure 2). There was also a significant difference in total 4-ringed PAH concentration between 1996-1999 and 2006-2008 ($p=0.0404$) (Figure 3). There was no significant difference in concentration for PAH with greater than 4 rings between any yearly grouping (Figure 4). The 4-ringed and >4-ringed PAH groups contributed the most by concentration to total PAH in Austin creek sediment. There were no significant differences in concentration of individual PAH between annual groupings.

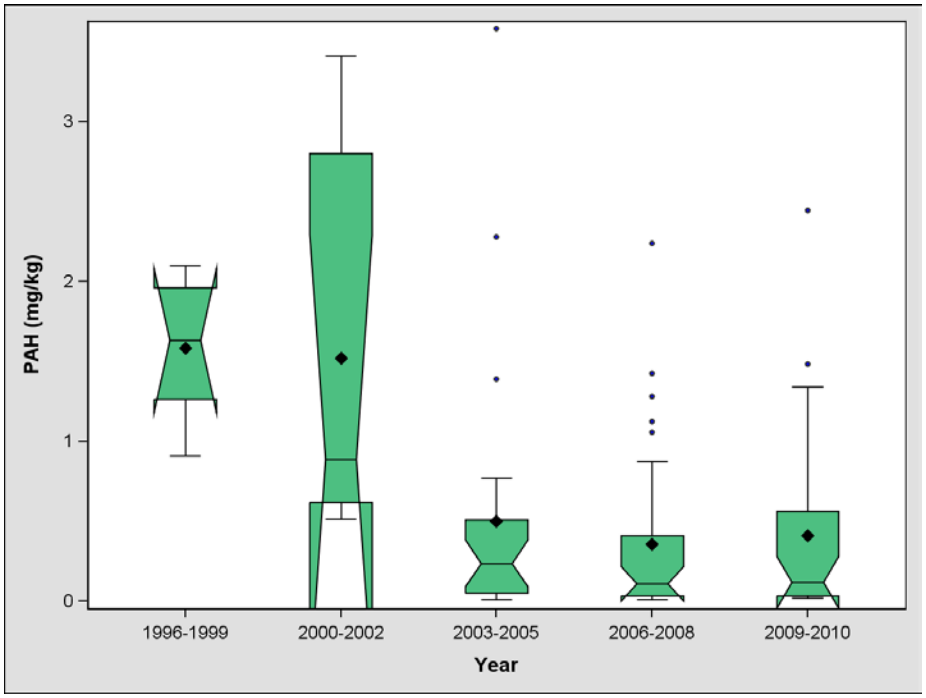

Figure 2: Box plot of 3-ringed PAH (mg/Kg) collected in EII sampling from 1996-2010. Black diamonds ◆represent means, notched lines ⧗ represent medians, and small circles •represent.

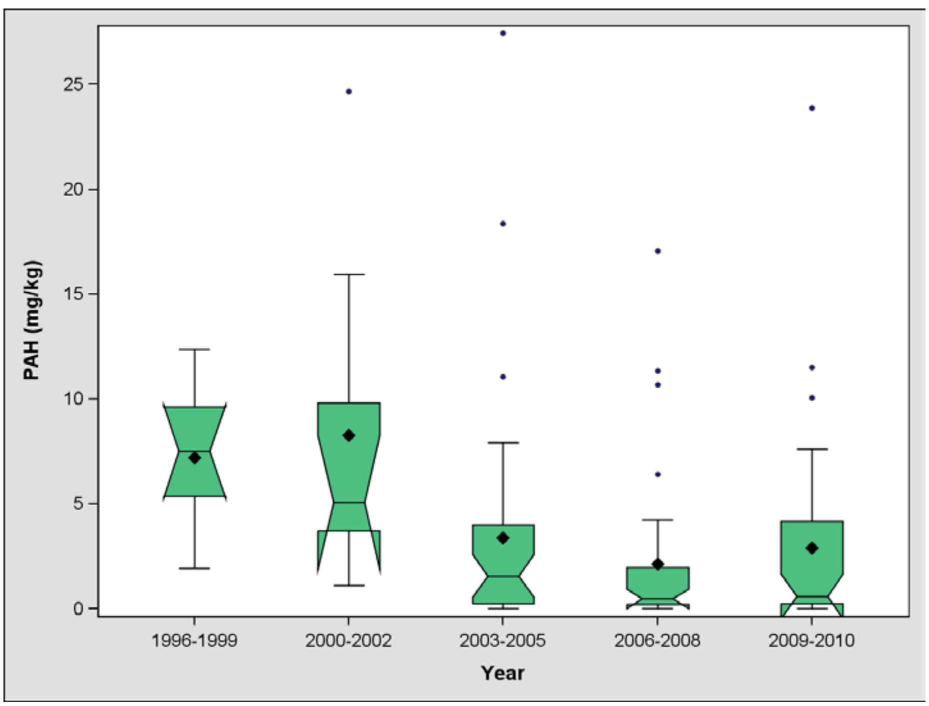

Figure 3: Box plot of 4-ringed PAH (mg/Kg) collected in EII sampling from 1996-2010. Black diamonds ◆represent means, notched lines ⧗ represent medians, and small circles •represent.

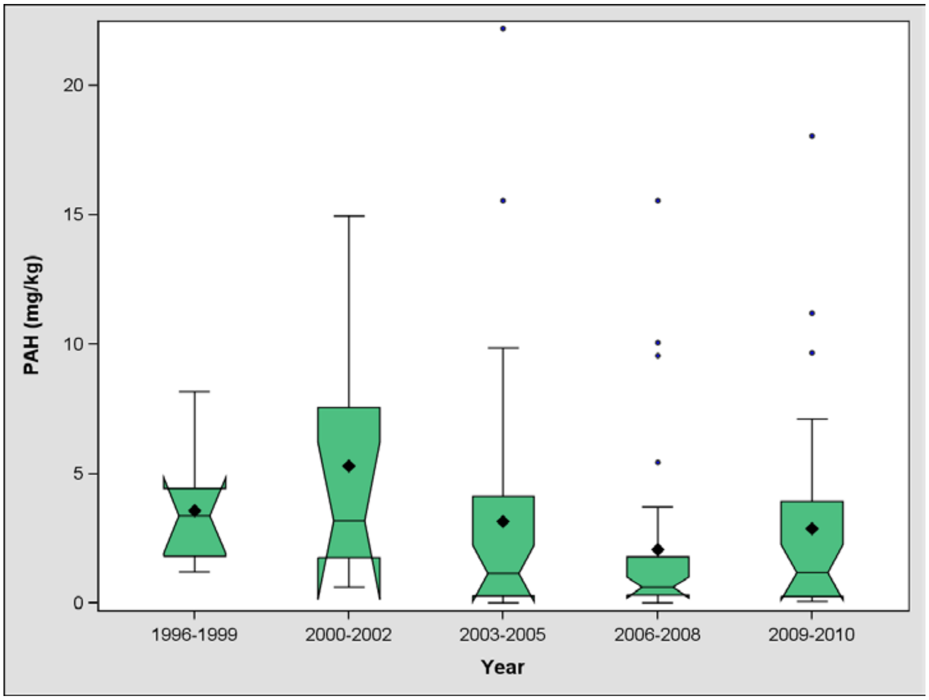

Figure 4: Box plot of >4-ringed PAH (mg/Kg) collected in EII sampling from 1996-2010. Black diamonds ◆represent means, notched lines ⧗ represent medians, and small circles •represent.

Commons Ford, Decker Creek, Harris Branch, Onion Creek, Running Deer, Turkey Creek, and Walter E. Long Lake watersheds did not contain any data points where PAH were detected, thus no temporal analysis was performed on sites within these watersheds. Cottonmouth, Country Club West, Cuernavaca, Dry, Gilleland, Johnson, Little Bear, North Fork Dry, Panther Hollow, and Rinard contained insufficient data points where PAH were detected so sites within these watersheds were also left out of temporal analysis for this report. Time plots of total PAH were constructed for the remainder of the watersheds of Austin.

Total PAH concentration showed no significant trends at individual sites within Bear Creek, Bear Creek West, Bee Creek, Blunn Creek, East Country Club Creek, Elm Creek, Fort Branch Creek, Lake Creek, Little Barton Creek, Little Bee Creek, Marble Creek, North Boggy Creek, Rattan Creek, Slaughter Creek, South Boggy Creek, South Fork Dry Creek, Tannehill Creek, Taylor Slough South, West Bouldin Creek, West Bull Creek, and Williamson Creek watersheds (Figures 5-25). Most of these sites were sampled only for the Environmental Integrity Index project and contained low total PAH concentration in all samples collected.

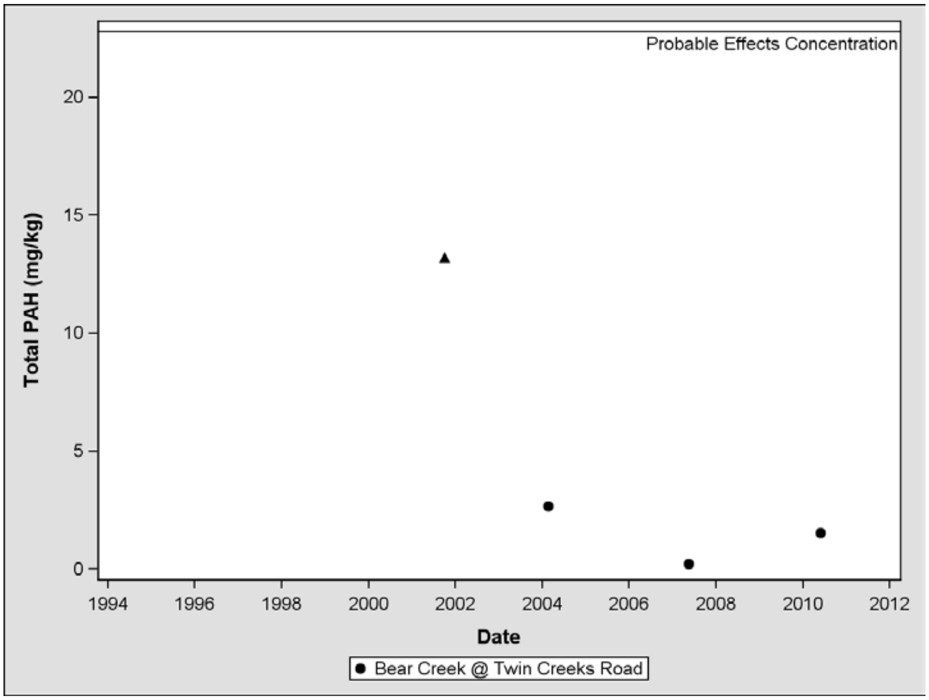

Figure 5: Total PAH (mg/Kg) within the Bear Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

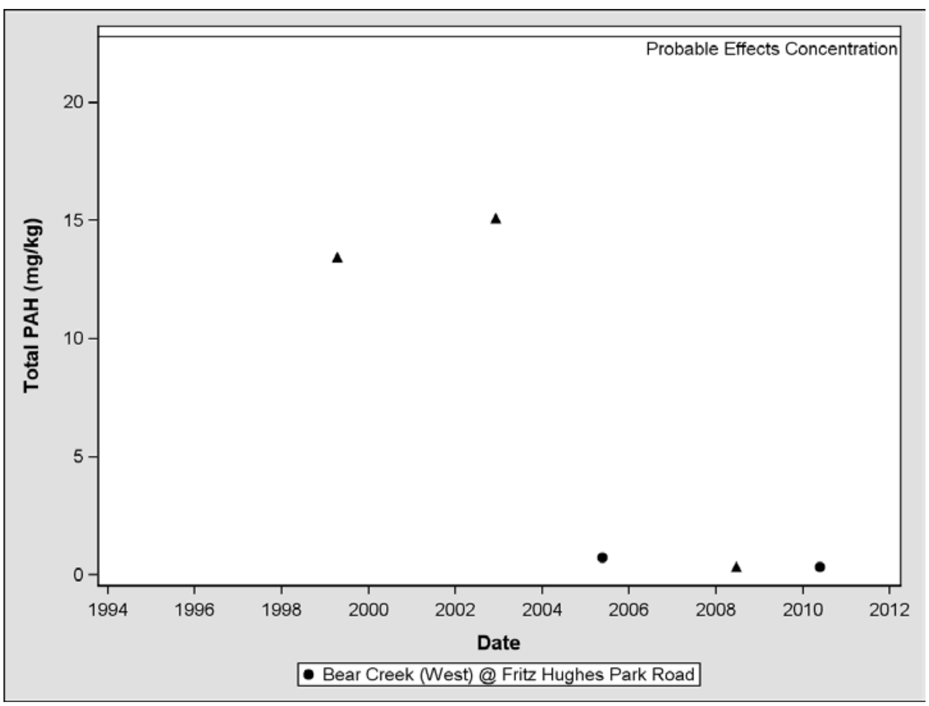

Figure 6: Total PAH (mg/Kg) within the Bear Creek West watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

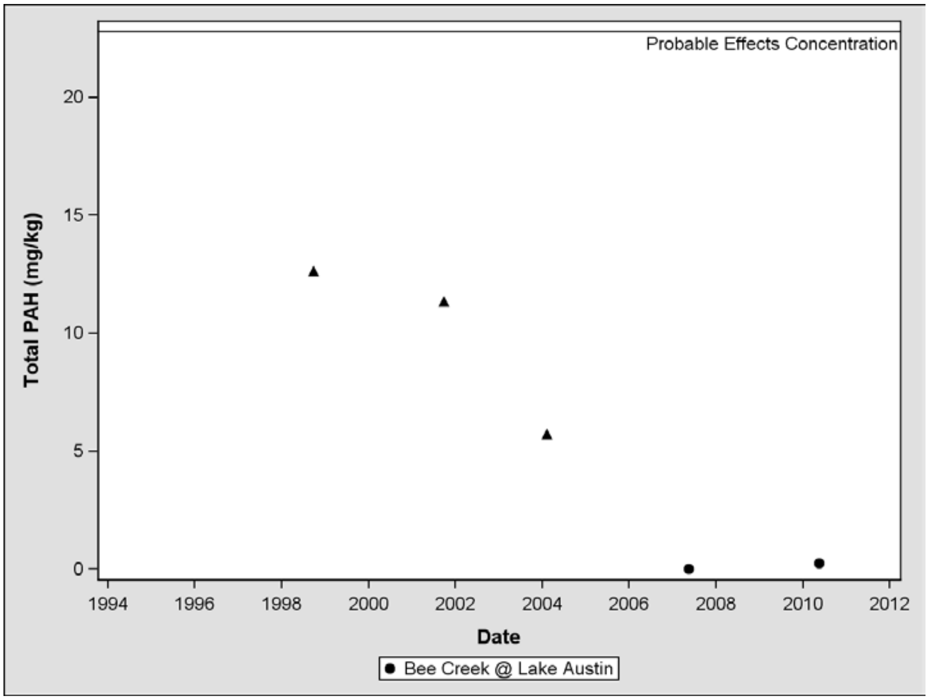

Figure 7: Total PAH (mg/Kg) within the Bee Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

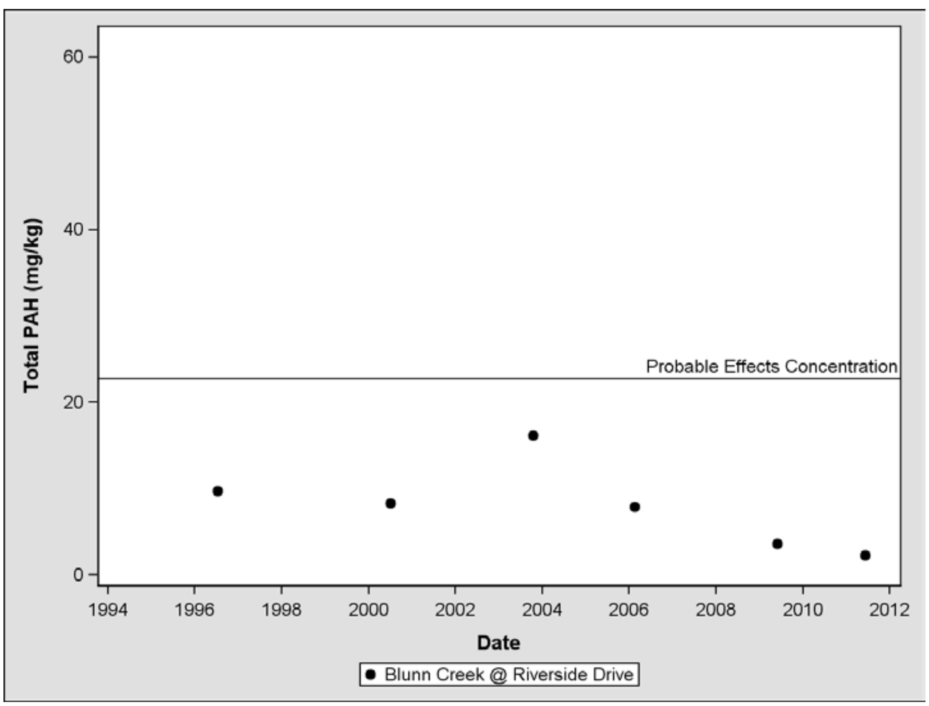

Figure 8: Total PAH (mg/Kg) within the Blunn Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

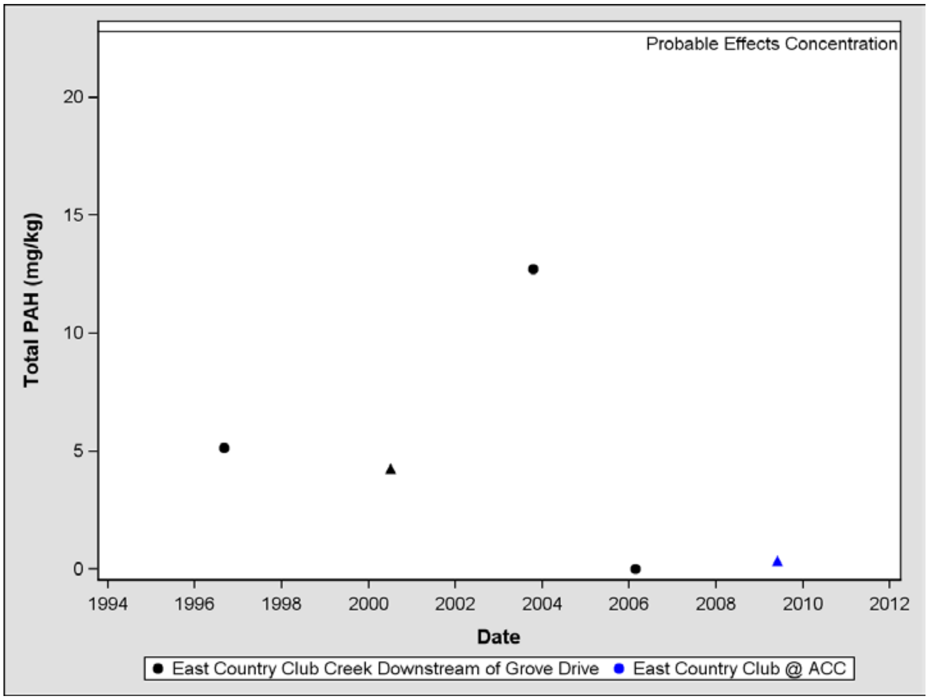

Figure 9: Total PAH (mg/Kg) within the East Country Club Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

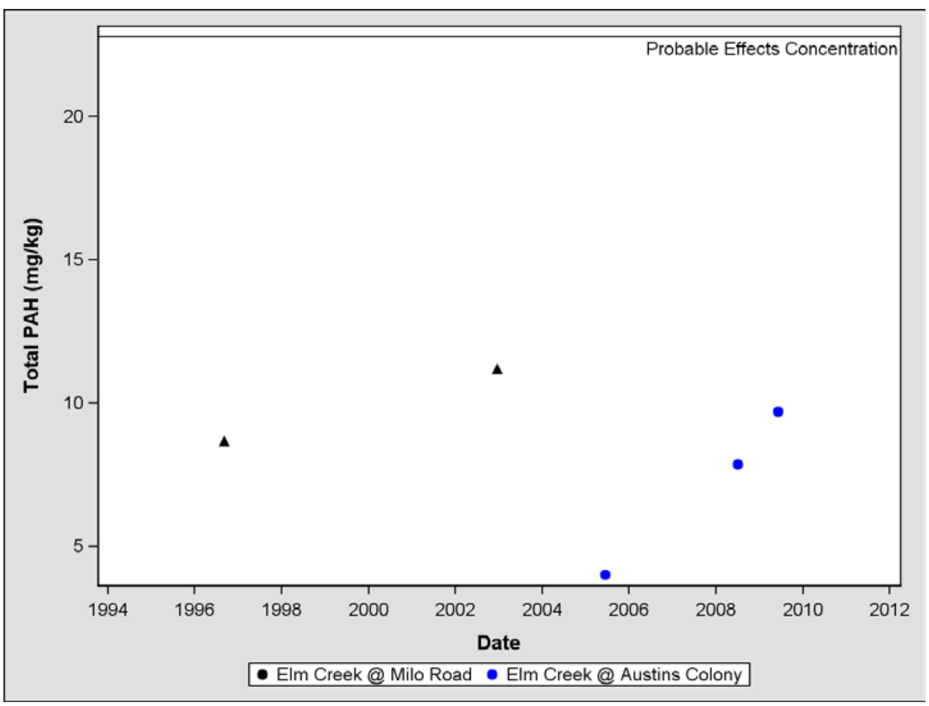

Figure 10: Total PAH (mg/Kg) within the Elm Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

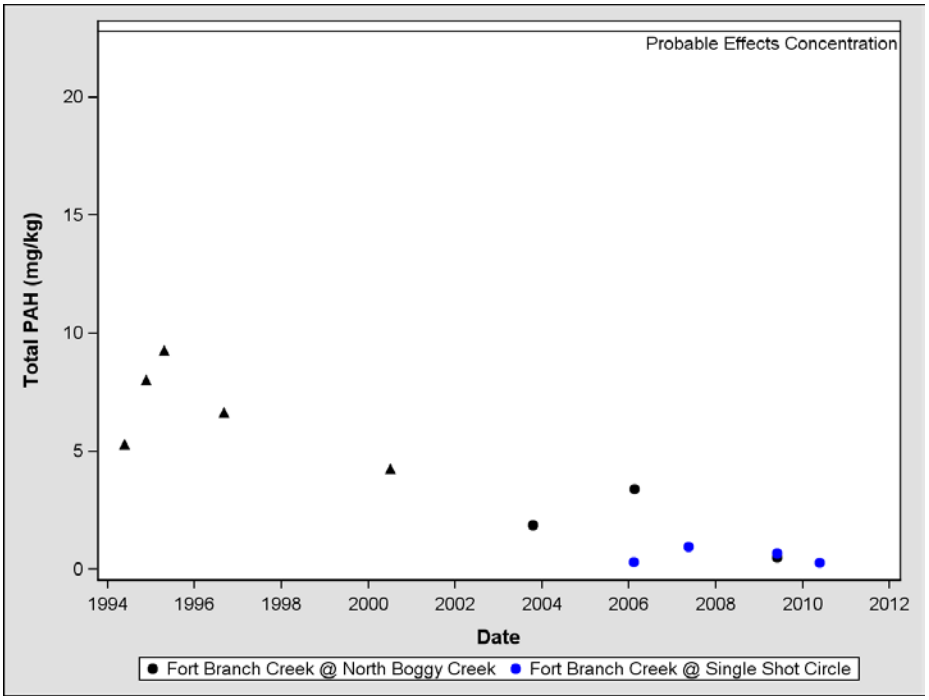

Figure 11: Total PAH (mg/Kg) within the Fort Branch Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

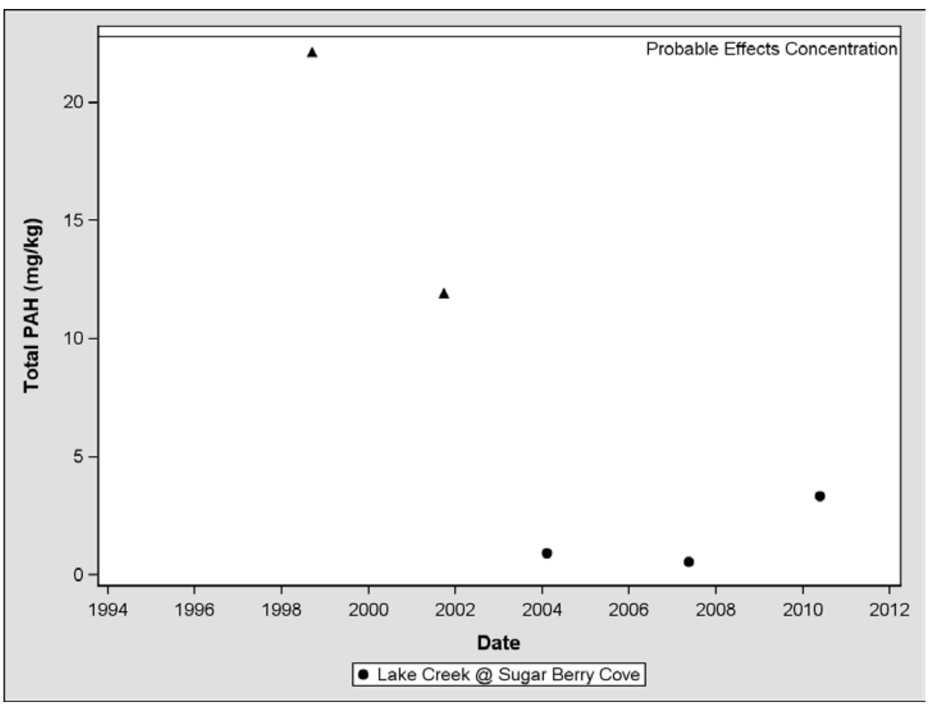

Figure 12: Total PAH (mg/Kg) within the Lake Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

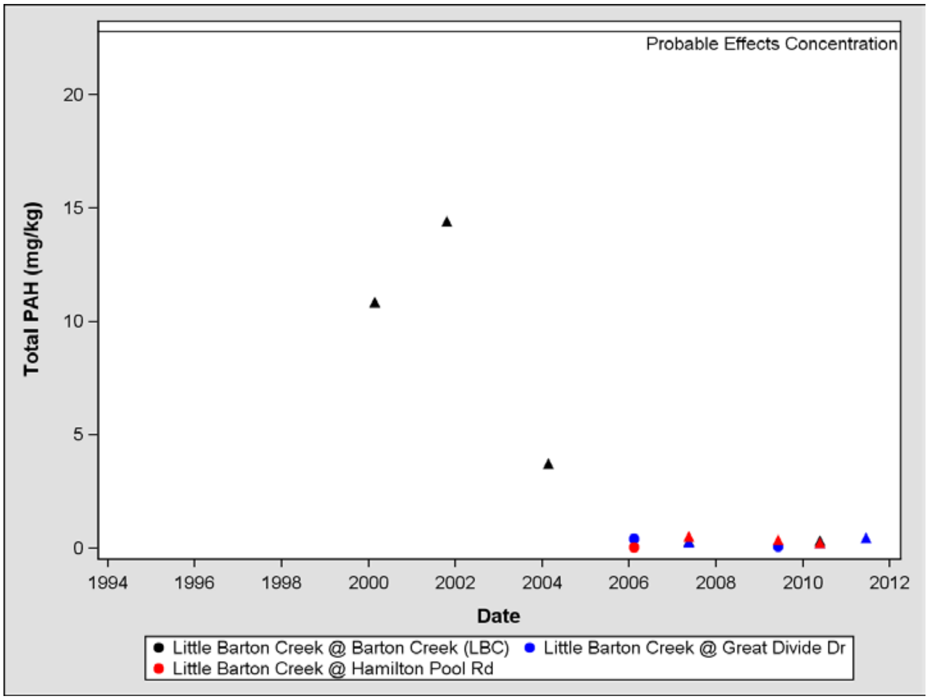

Figure 13: Total PAH (mg/Kg) within the Little Barton Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

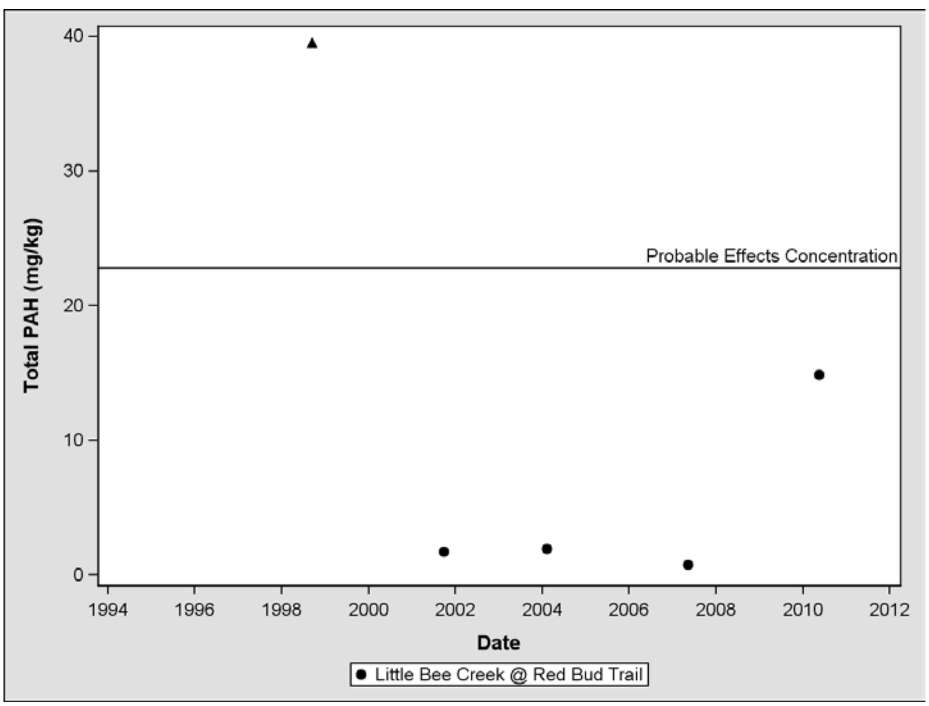

Figure 14: Total PAH (mg/Kg) within the Little Bee Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

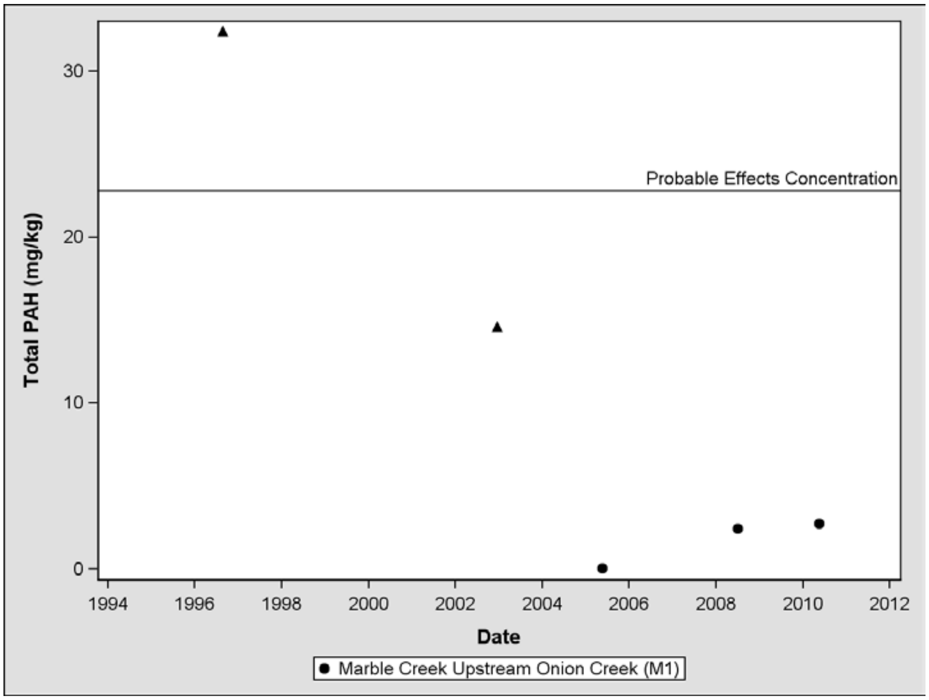

Figure 15: Total PAH (mg/Kg) within the Marble Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

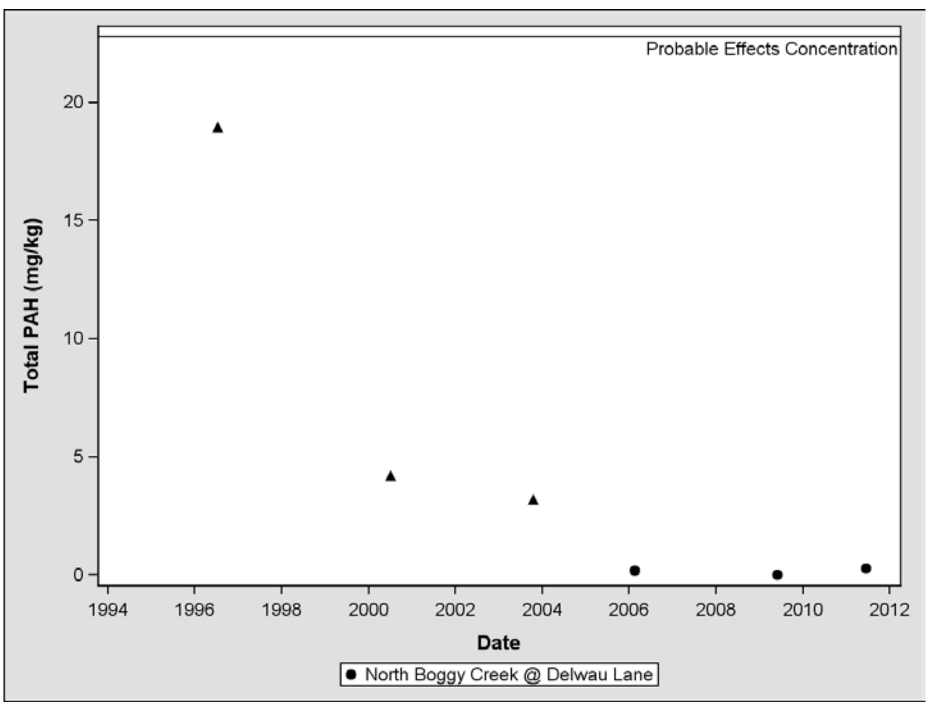

Figure 16: Total PAH (mg/Kg) within the North Boggy Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

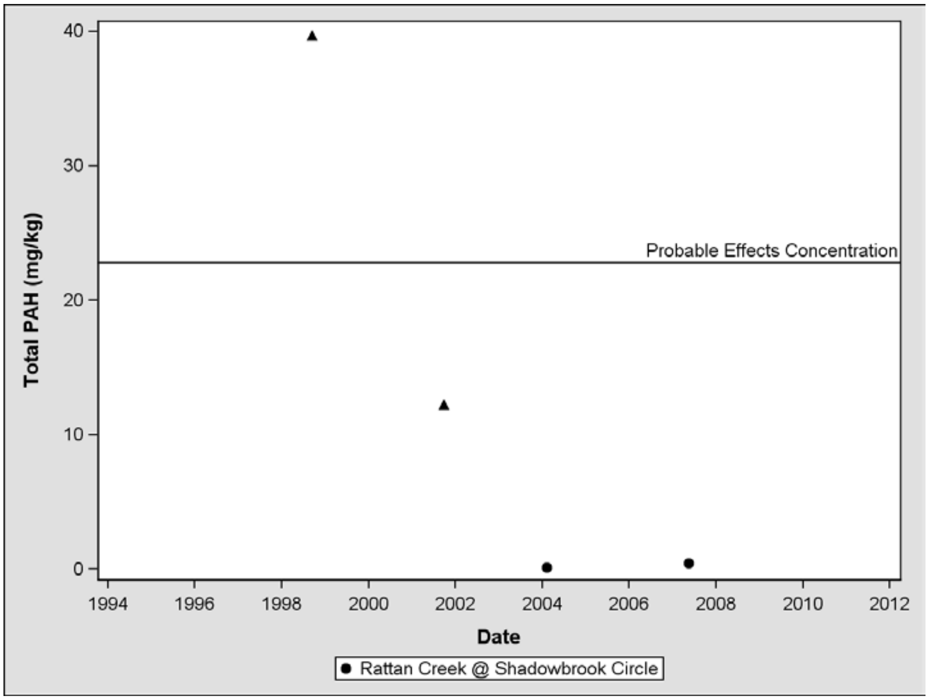

Figure 17: Total PAH (mg/Kg) within the Rattan Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

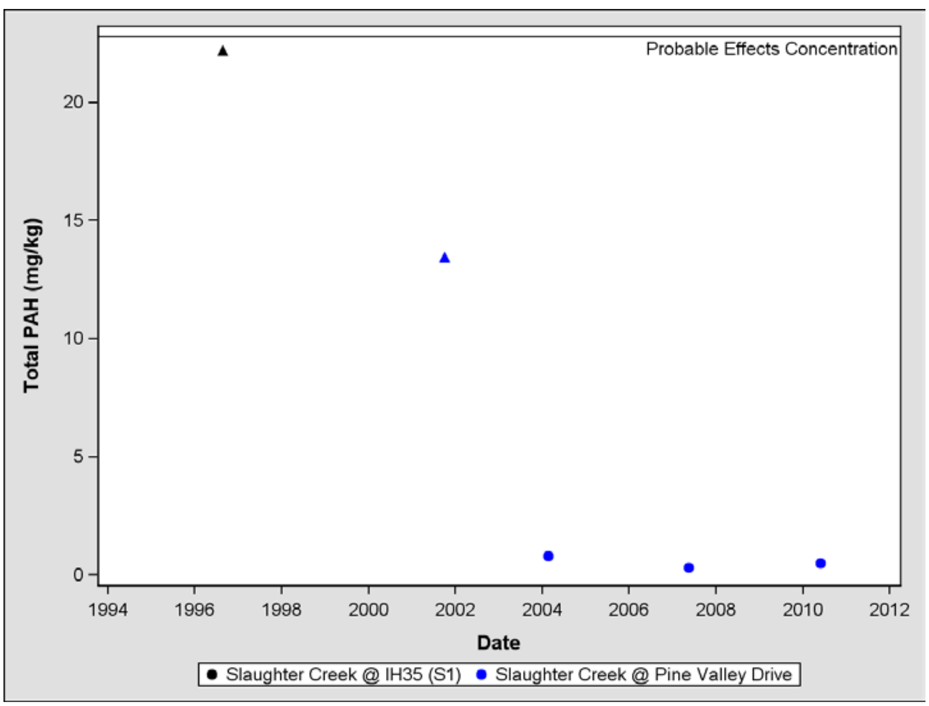

Figure 18: Total PAH (mg/Kg) within the Slaughter Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

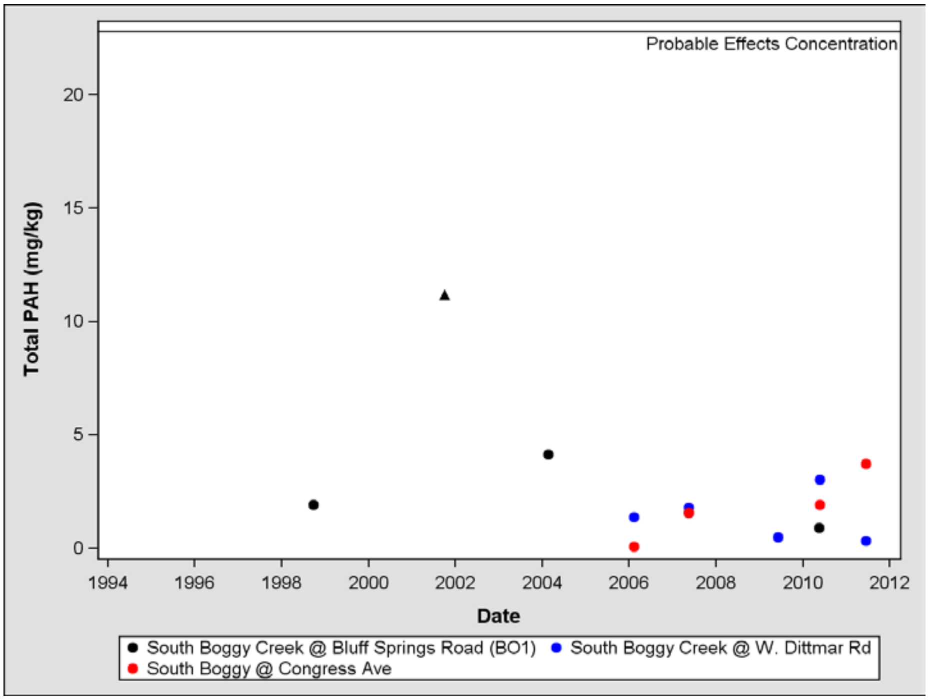

Figure 19: Total PAH (mg/Kg) within the South Boggy Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

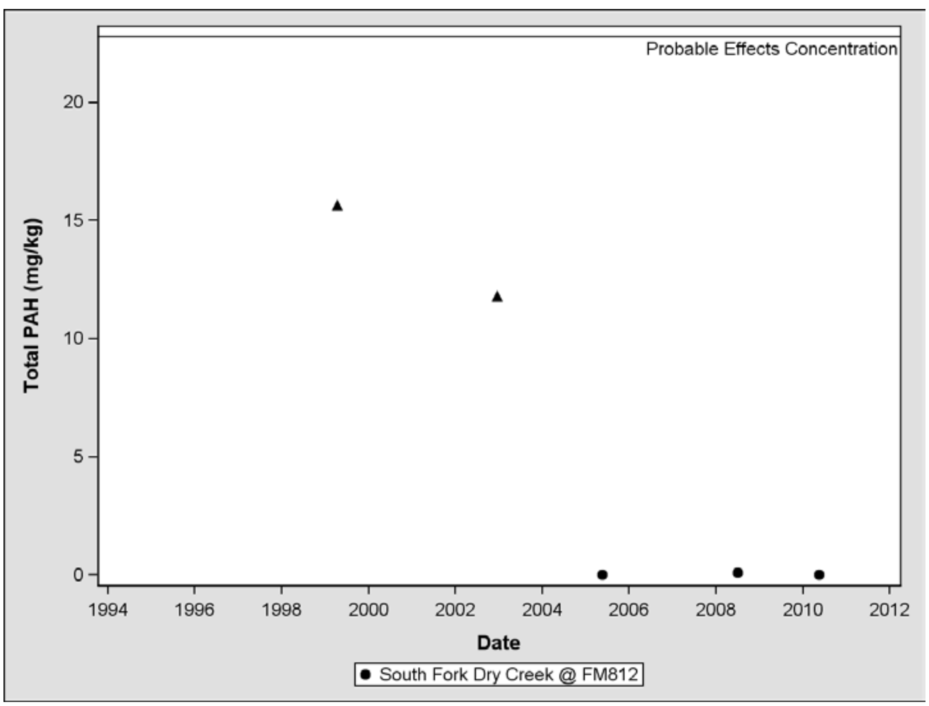

Figure 20: Total PAH (mg/Kg) within the South Fork Dry Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

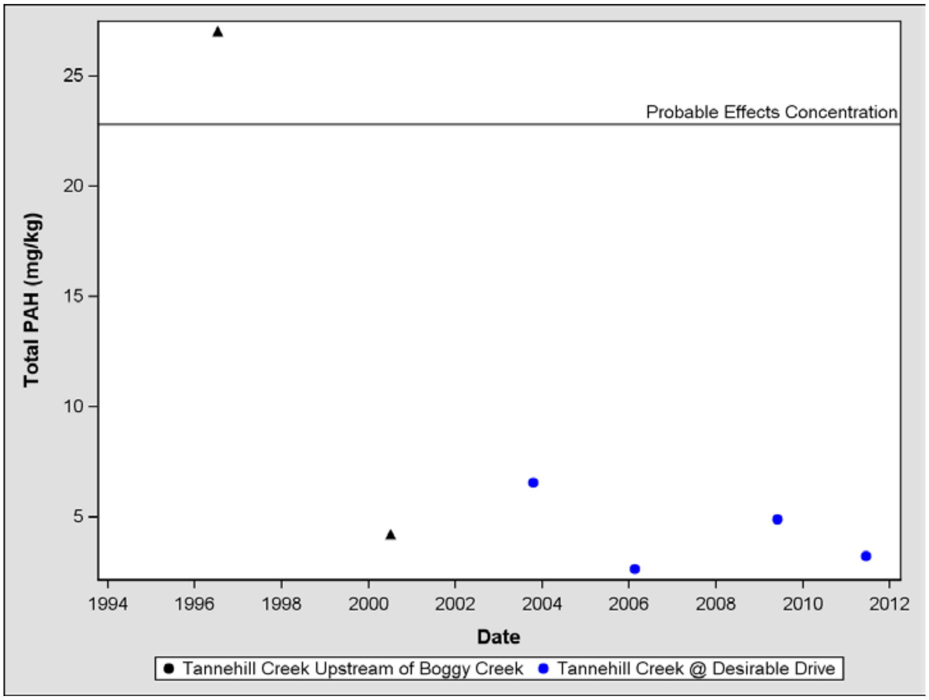

Figure 21: Total PAH (mg/Kg) within the Tannehill Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

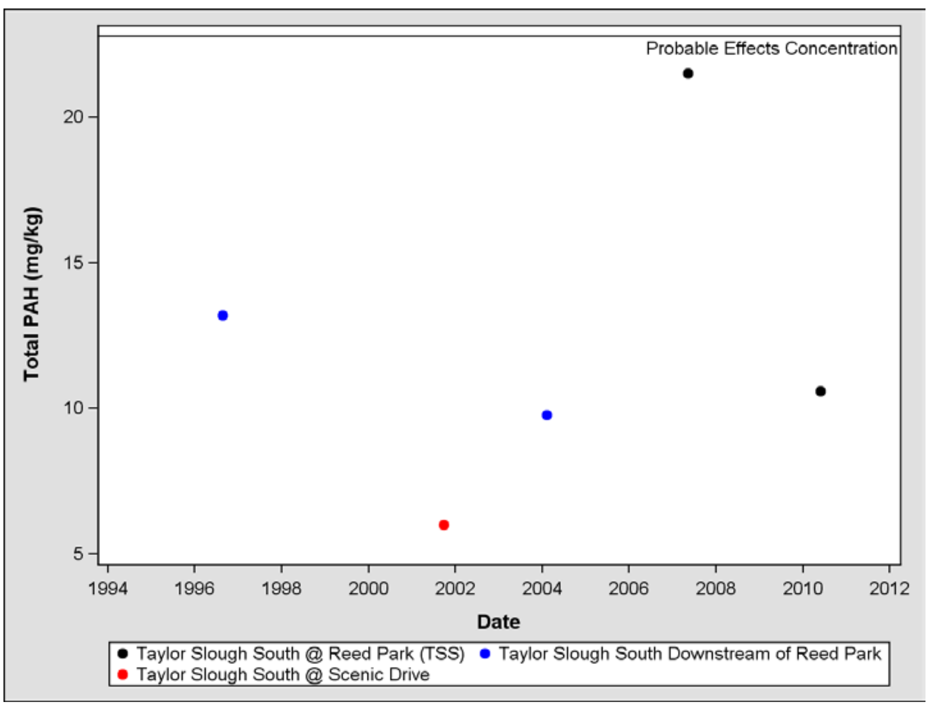

Figure 22: Total PAH (mg/Kg) within the Taylor Slough South watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

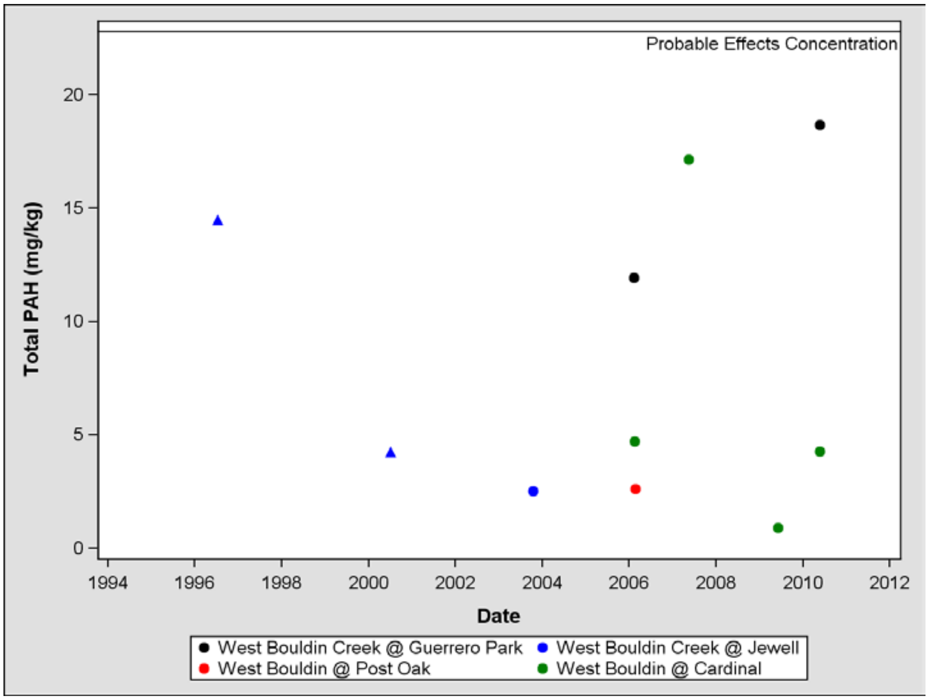

Figure 23: Total PAH (mg/Kg) within the West Bouldin Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

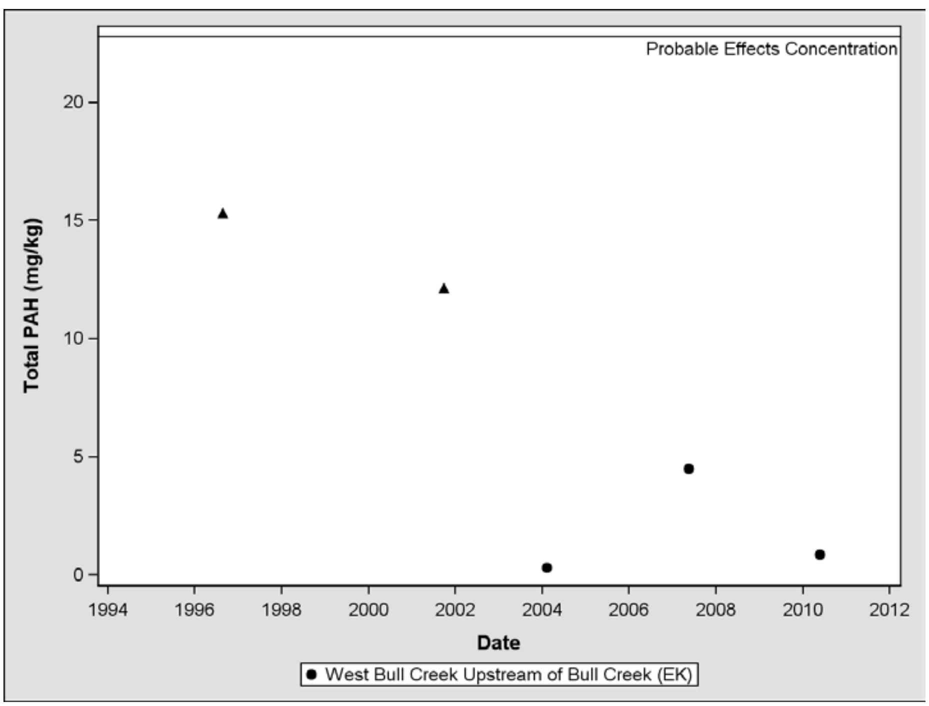

Figure 24: Total PAH (mg/Kg) within the West Bull Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

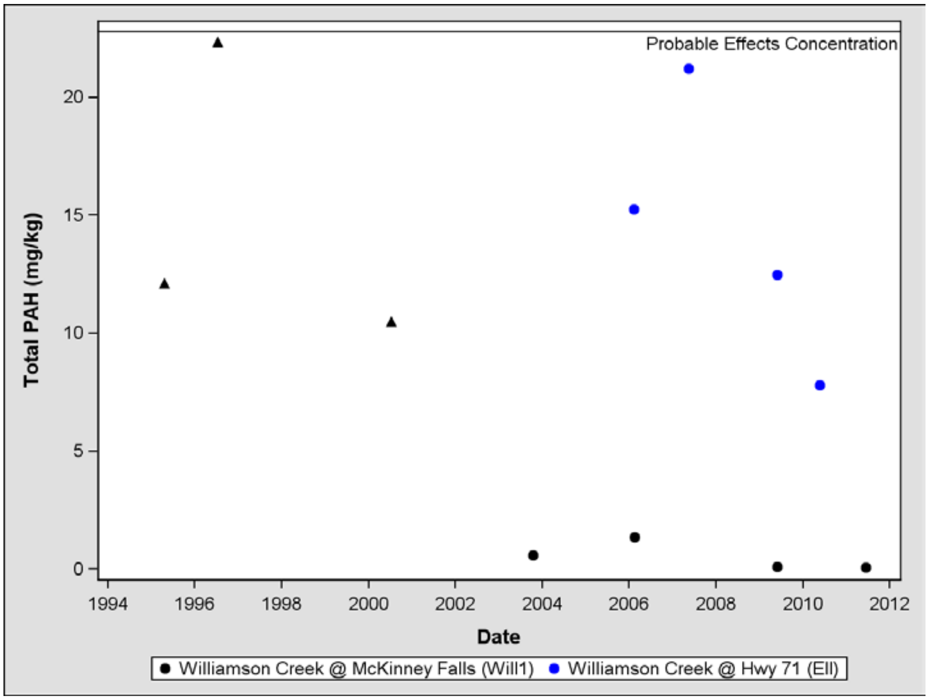

Figure 25: Total PAH (mg/Kg) within the Williamson Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

Significant temporal trends in total PAH concentration only existed within the Barton Creek watershed ($p=0.0004$, $R^2=0.4021$) (Figure 26). Prior to 2004, total PAH concentration was often well above the Probable Effects Concentration in Barton Creek upstream of Barton Springs Pool. Recent sediment samples taken at this site showed that the total PAH concentration has stayed well below the PEC. Two actions that could have contributed to this improvement include a voluntary coal-tar ban prior to the ban set forth by council and the construction of a water quality control built to intercept storm water runoff up gradient of the sampling location at a large parking lot known to be sealed with coal-tar based sealant.

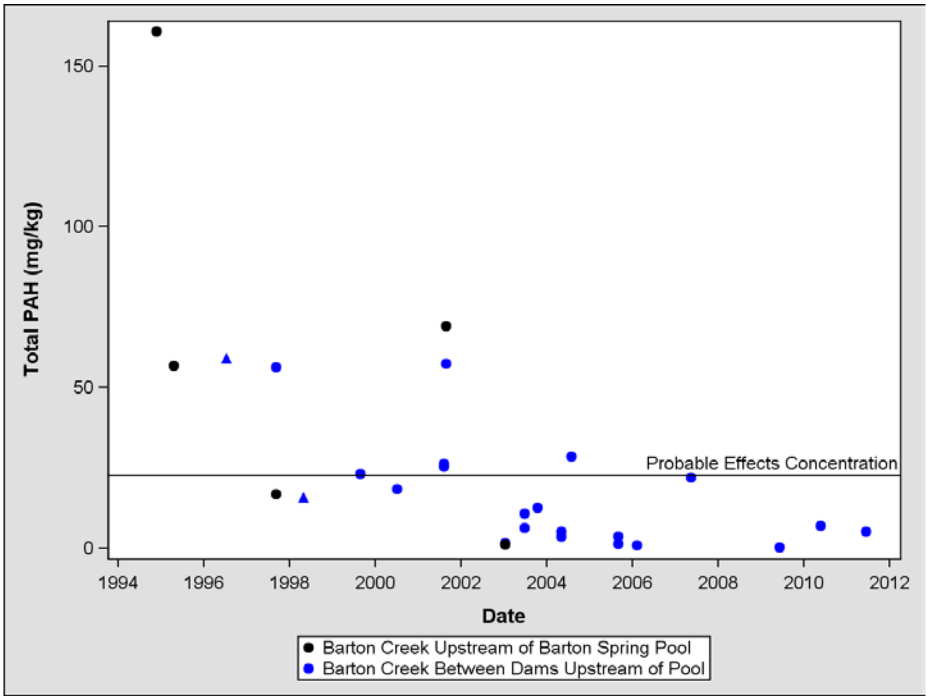

Figure 26: Total PAH (mg/Kg) within the Barton Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

While no significant trends were found within the Shoal Creek watershed, there was an instance of high total PAH concentration in 1995 (Figure 27). Recent samples have shown that total PAH concentration in Shoal Creek have remained below the Probable Effect Concentration, even though this is a highly urbanized watershed.

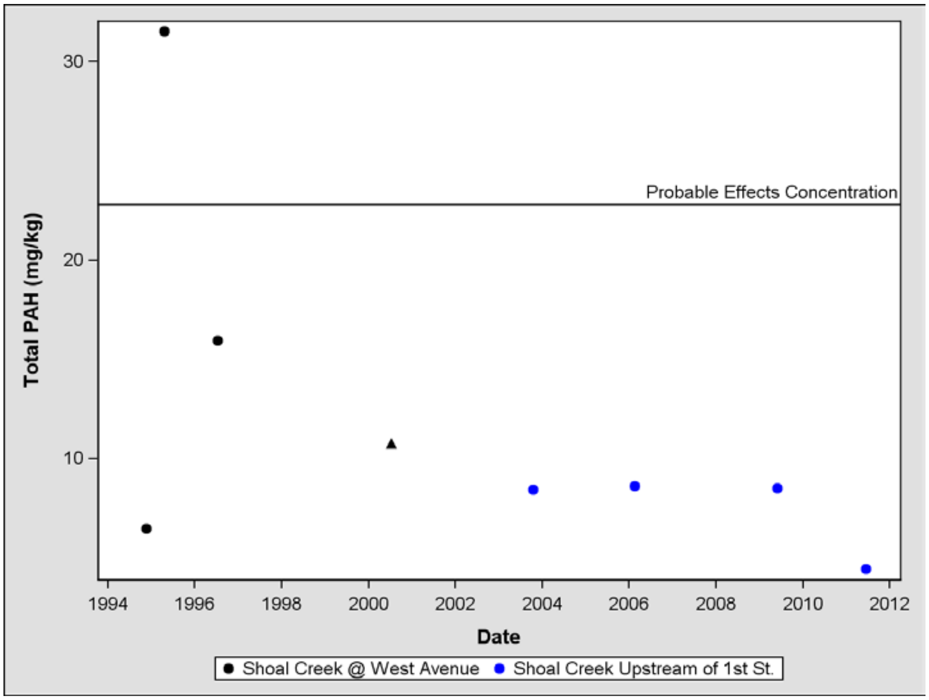

Figure 27: Total PAH (mg/Kg) within the Shoal Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

The remaining watersheds in Austin did not show any significant trend over time for total PAH but there have been more recent cases of concentrations above the PEC. Bull Creek @ Loop 360 was above the PEC in 2009 (Figure 28). While the two most current samples taken at the Loop 360 crossing have shown decreasing concentrations, the levels were higher than at other Bull Creek sites. This site is currently the EII sediment site for Bull Creek and will continue to be monitored for PAH in the future. As the concentration of PAH varied greatly at this site, it is recommended that this site be monitored for total PAH even if the EII site location changes. Other sites within this watershed were never above this concentration.

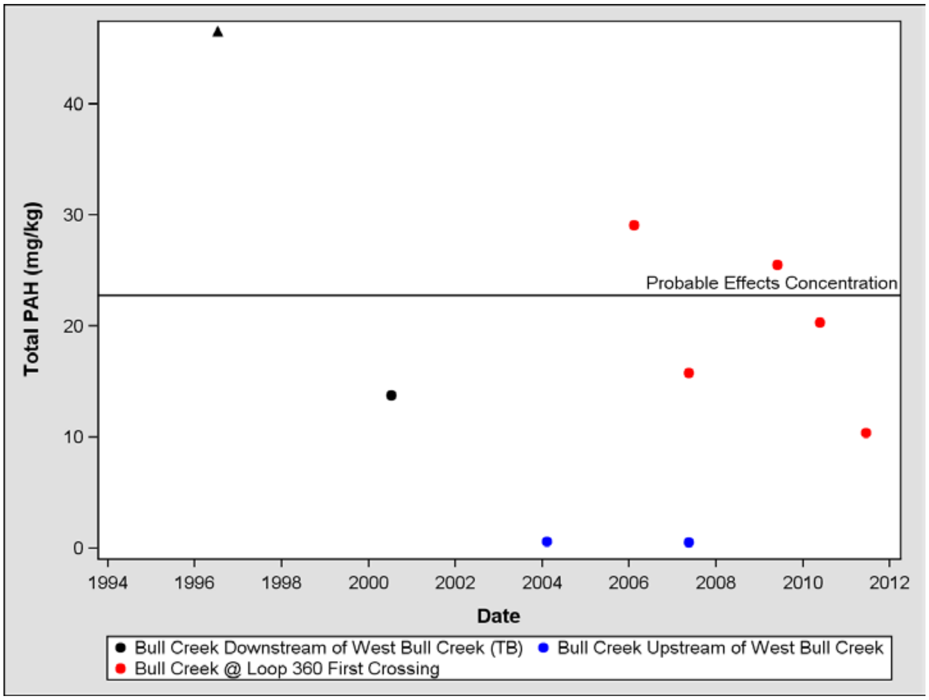

Figure 28: Total PAH (mg/Kg) within the Bull Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

Another site that had high concentrations of PAH but was variable over time was Buttermilk Creek at Little Walnut Creek (Figure 29). The most recent sample suggested that the concentrations were well below the PEC; however, in 2009 the concentration of total PAH was above the PEC at this site. Carson Creek at US 183 was another site where total PAH concentration was above the PEC (Figure 30). Concentrations at this site remained high but were below the PEC in the most recent samples. Total PAH concentrations were not high at other sites on Carson Creek.

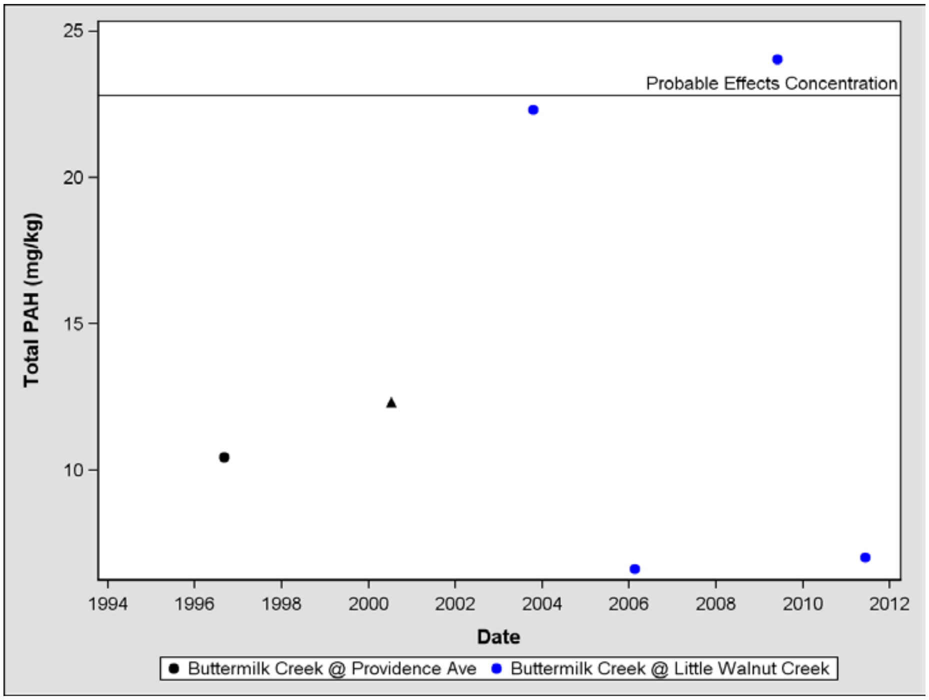

Figure 29: Total PAH (mg/Kg) within the Buttermilk Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

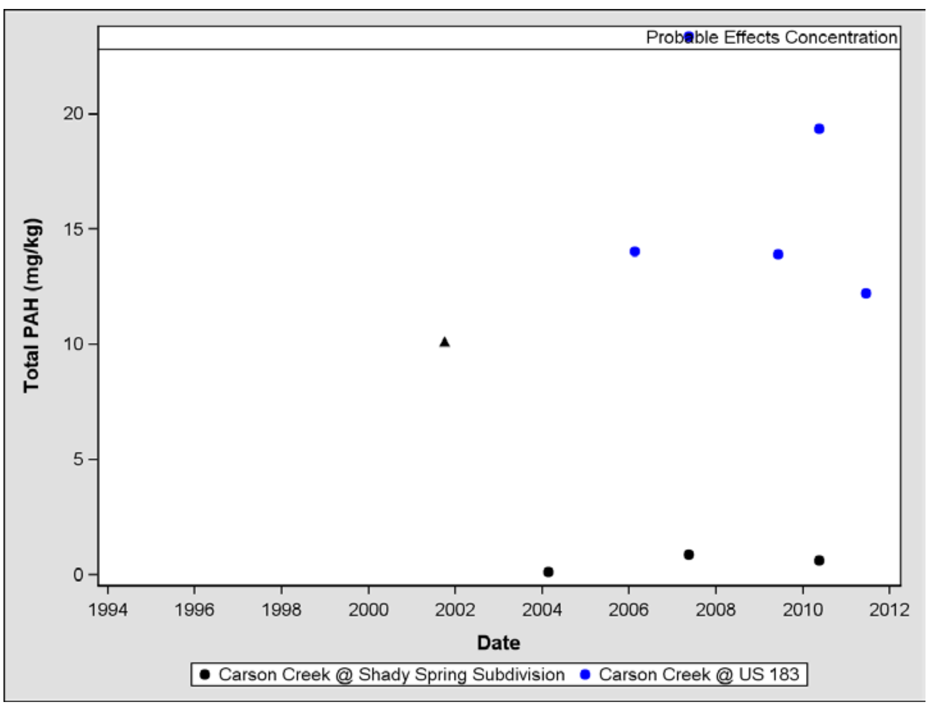

Figure 30: Total PAH (mg/Kg) within the Carson Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

Other sites of major interest included Dry Creek North at Highland Pass, Eanes Creek at Camp Craft, East Bouldin Creek Downstream of West Alpine, East Bouldin Creek at Elizabeth, East Bouldin Creek at Post Oak, Harper's Branch at Woodland Ave., Little Walnut at Golden

Meadow, Taylor Slough North at Pecos, Waller Creek at Pipe Upstream of 24^{th} St., and Walnut Creek at Metric (Figures 31 – 38). All of these sites have multiple recent samples where the total PAH concentration is well above the PEC. Eanes Creek and Harper's Branch had the highest concentrations of these sites, and concentrations at Harper's Branch may be increasing over time even though there was not a significant trend.

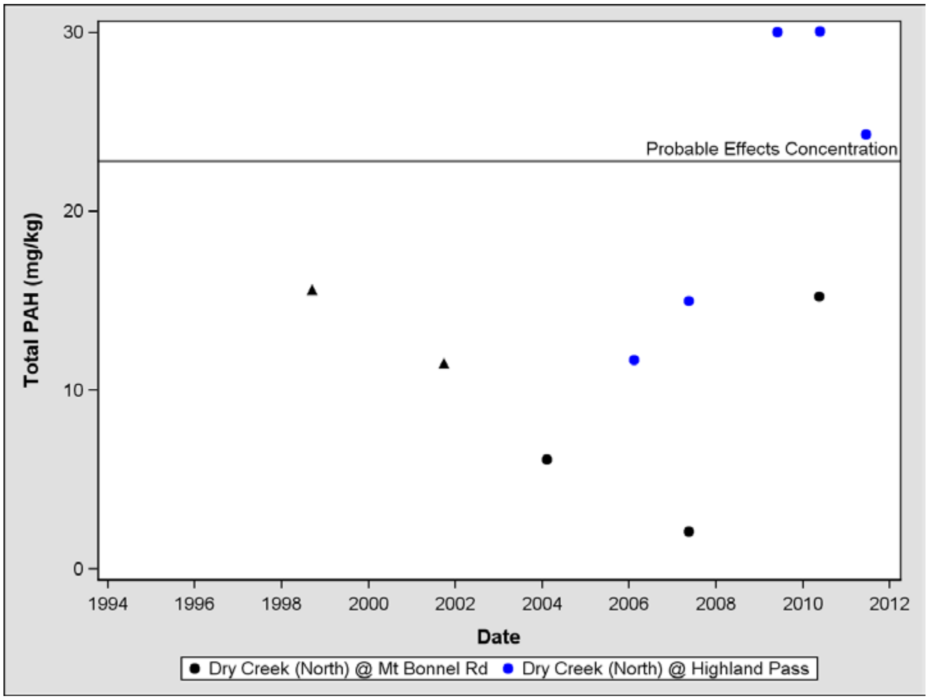

Figure 31: Total PAH (mg/Kg) within the Dry Creek North watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

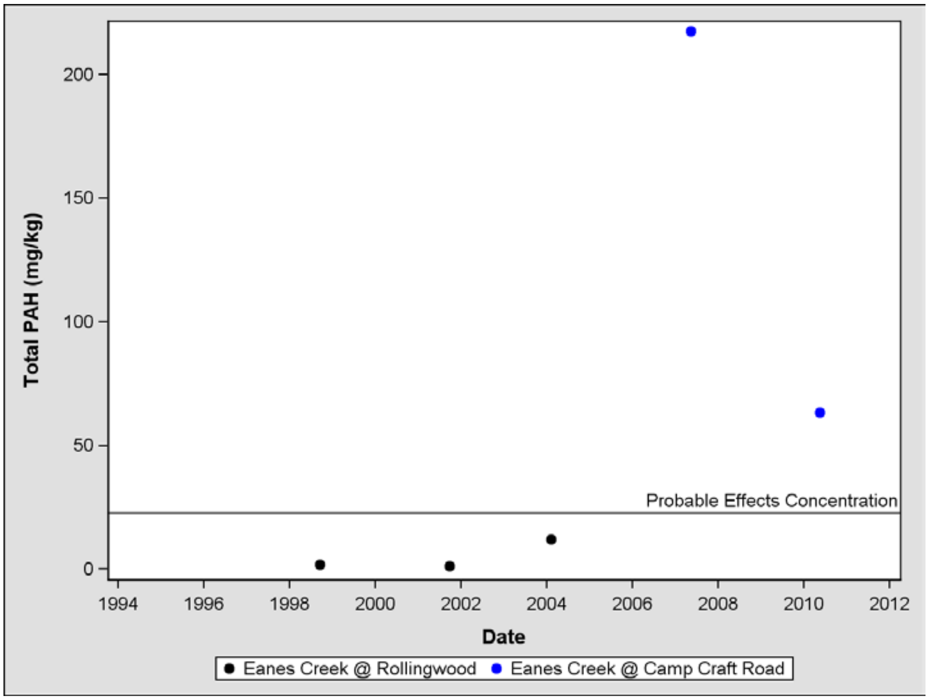

Figure 32: Total PAH (mg/Kg) within the Eanes Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

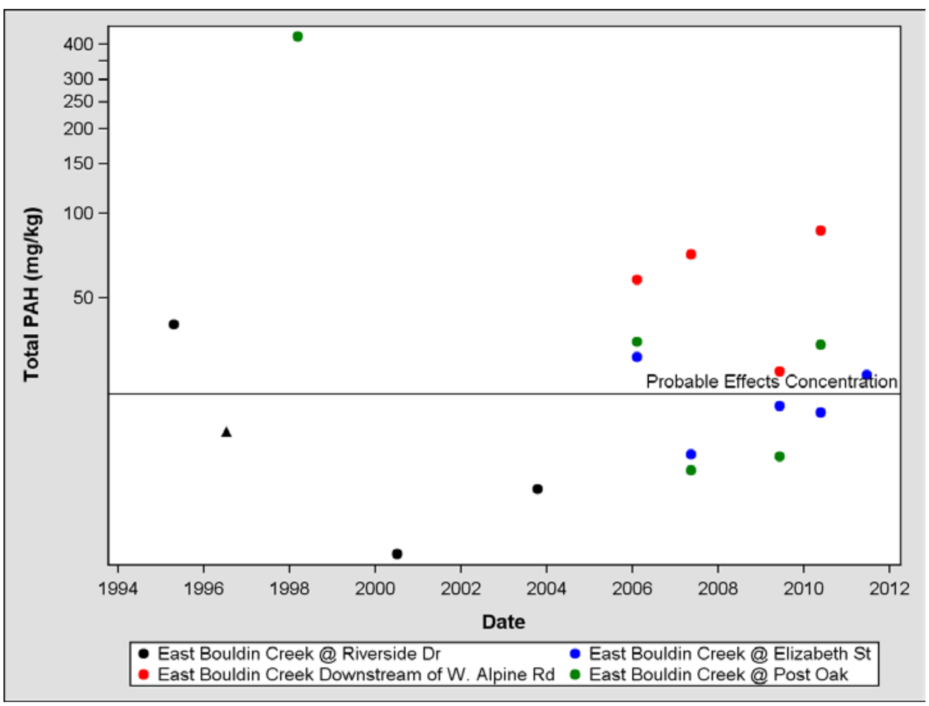

Figure 33: Total PAH (mg/Kg) within the East Bouldin Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

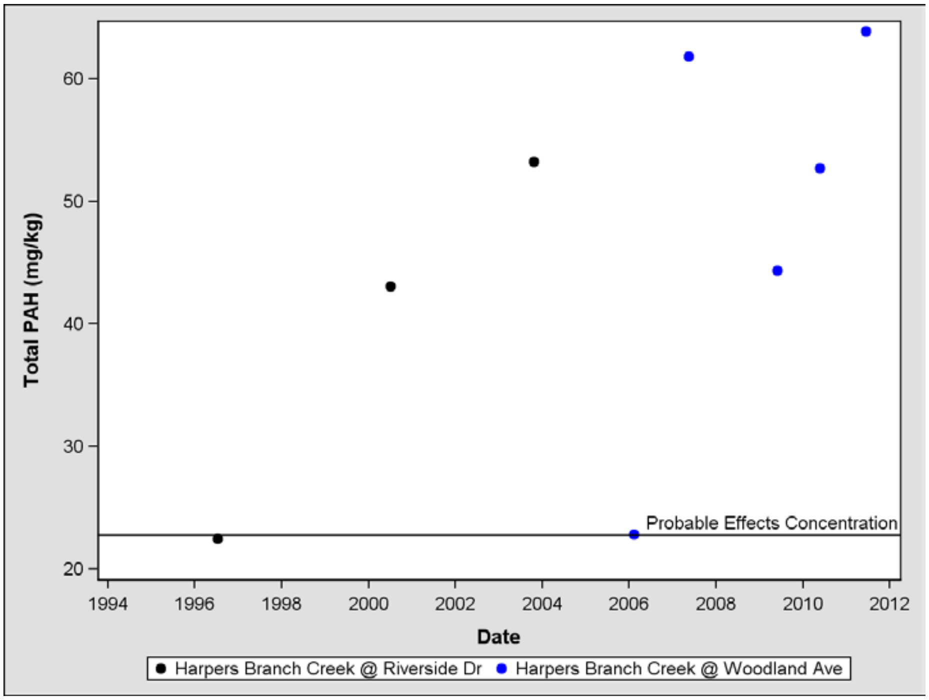

Figure 34: Total PAH (mg/Kg) within the Harper's Branch watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

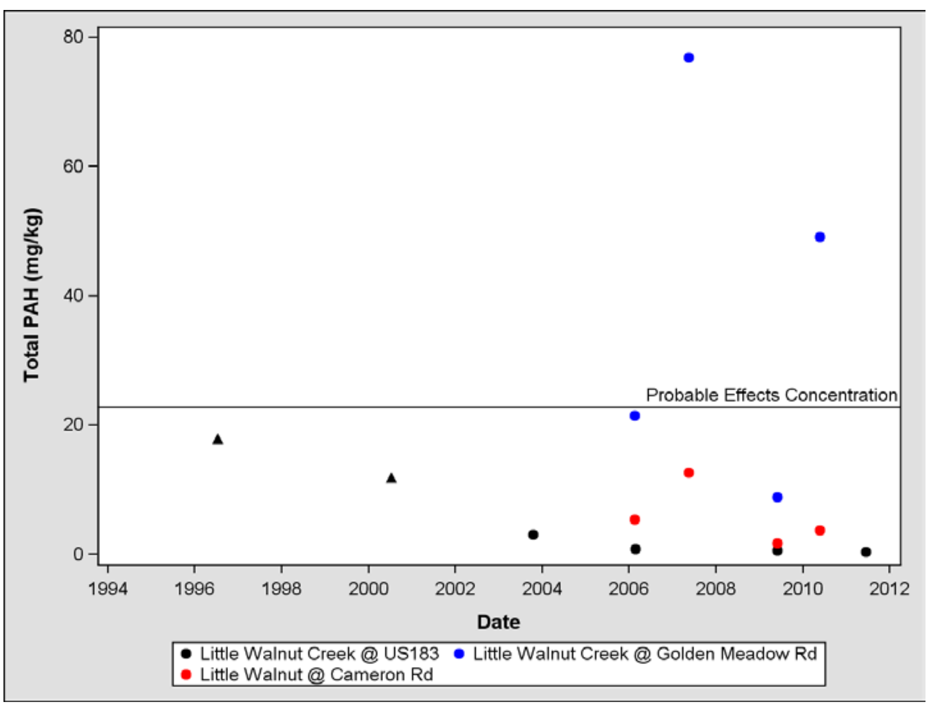

Figure 35: Total PAH (mg/Kg) within the Little Walnut Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

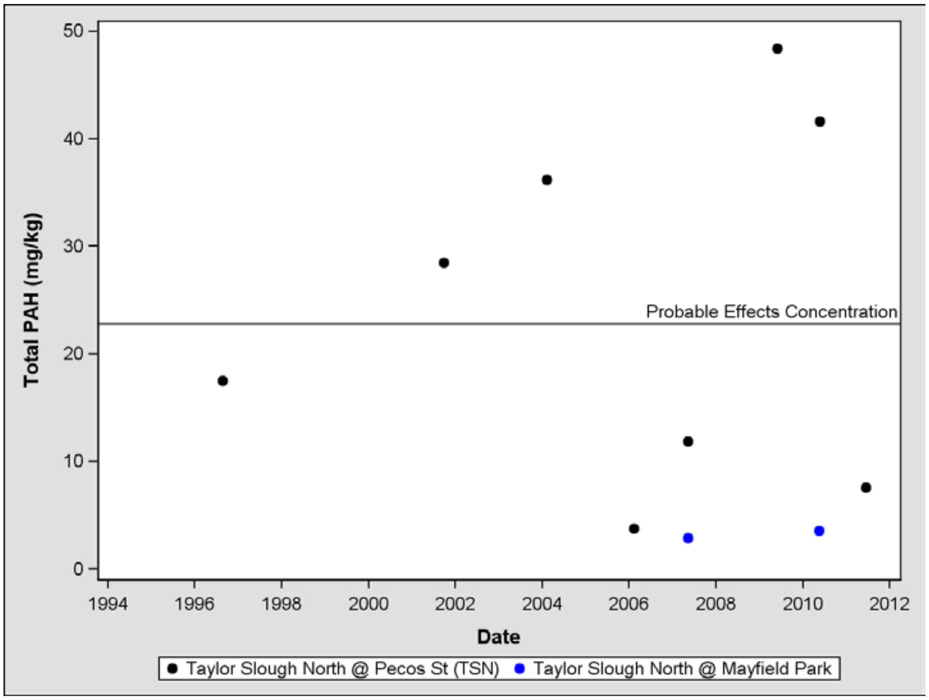

Figure 36: Total PAH (mg/Kg) within the Taylor Slough North Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

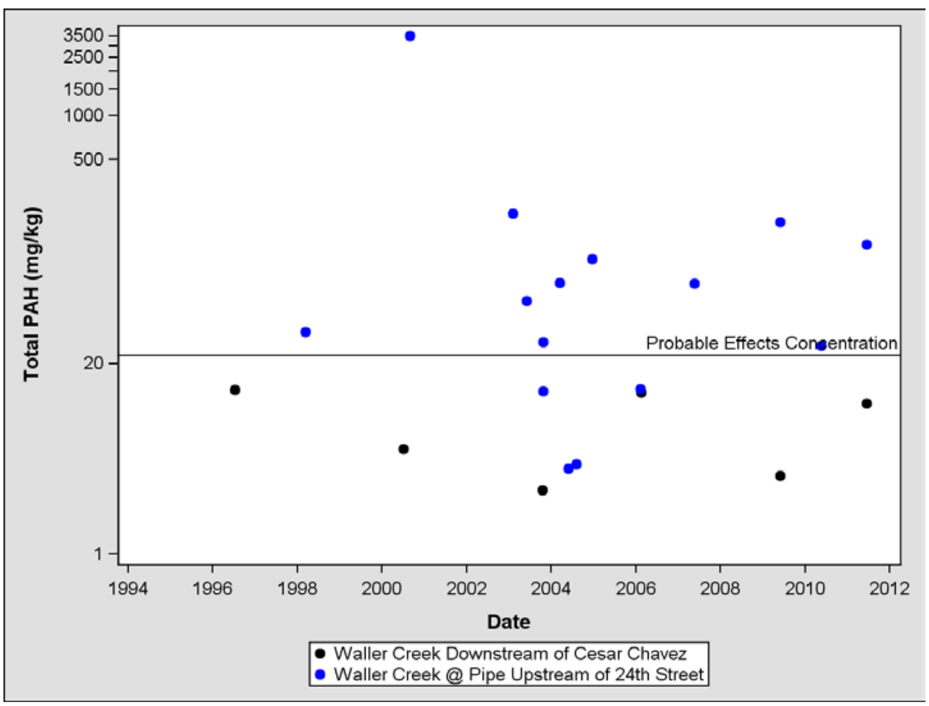

Figure 37: Total PAH (mg/Kg) within the Waller Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

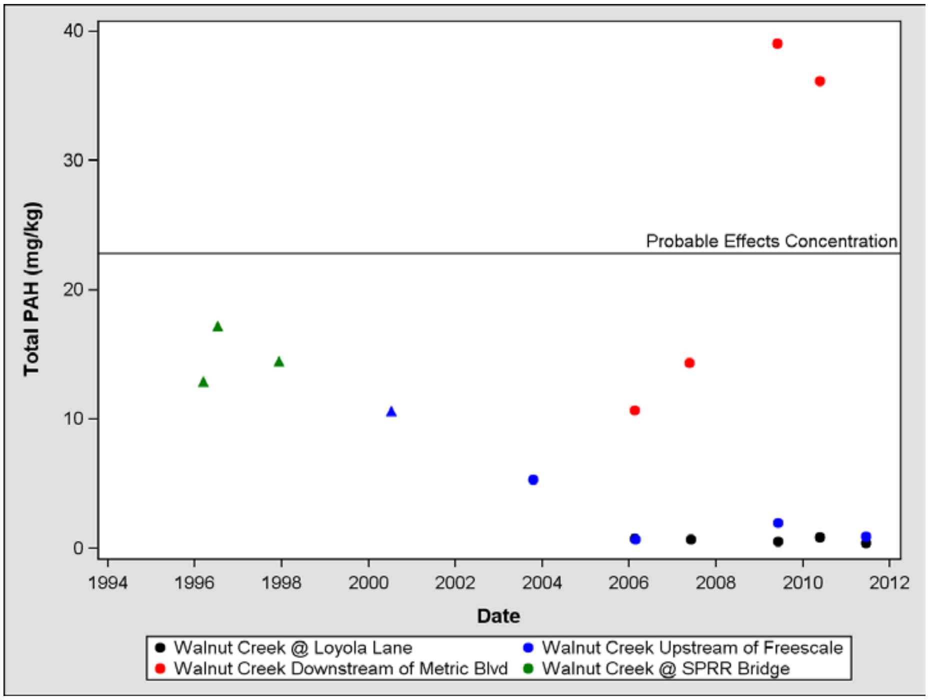

Figure 38: Total PAH (mg/Kg) within the Walnut Creek watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

Sediment in Lady Bird Lake at the Basin was thought to be a accumulation of sediment that traveled through most of the Austin creeks and lakes. As such, concentrations of total PAH at this site should represent the overall PAH level loaded to sediment in Austin. Total PAH in Lady Bird Lake at the Basin has not gone above 15 mg/Kg in samples collected since 2004 (Figure 39).

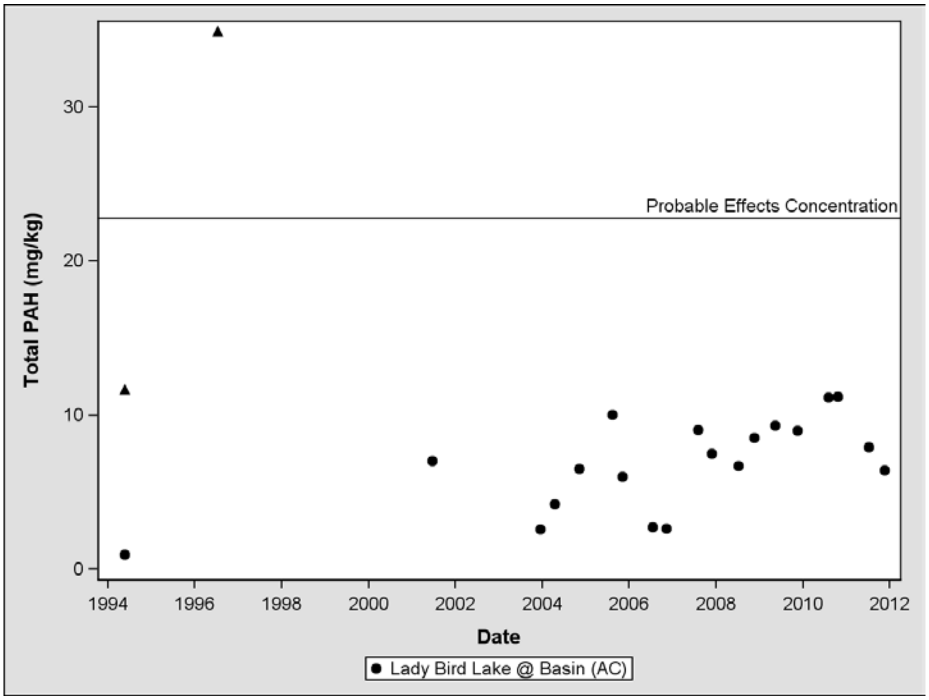

Figure 32: Total PAH (mg/Kg) within the Lady Bird Lake watershed. Circles represent a normal data point while triangles represent concentrations below detection level.

Conclusions

The concentration of 3-ringed and 4-ringed PAH in Austin creeks was lower in recent years than it was in 1996-1999. The same type of PAH seemed to be lower in recent years than in 2000-2002 as well, but this was not supported statistically. The concentrations of 2-ringed and >4-ringed PAH was about the same throughout this time period, thus the total PAH concentration was lower in recent years than in 1996-1999 (and possibly lower in recent years compared to 2000-2002). This implies that the sources of PAH have been limited or reduced through the majority of the Austin area. Without a constant source of PAH contamination the 3-ringed PAH can readily volatilize or be degraded by microorganisms (Moore and Ramamoorthy 1984, Mrozik et al 2003, Leduc et al 1992, Cerniglia 1992). The 4-ringed PAH are degraded more slowly and the >4-ringed PAH are degraded the slowest (Cerniglia 1992, Krivobok et al 2003). As the higher molecular weight PAH have not decreased through the time period, they will probably require more time for detectable biodegradation to occur.

While previous studies have shown that runoff from parking lots sealed with coal-tar sealant could contaminate the sediment of nearby creeks, it appears that the majority of sites sampled for the Environmental Integrity Index were not contaminated to levels above the Probable Effect Concentration. The ban of coal-tar sealant should help minimize one of the larger PAH sources and prevent PAH concentrations from increasing. One site that should be noted is Barton Creek above Barton Springs Pool. This site is immediately upstream of Barton Springs, which is occupied by the endangered Barton Springs Salamander and a recreational mecca for Austin citizens. Thus it is important for PAH levels to remain at a level that will not affect human or salamander health near this location. In the past, concentration of PAH has been above the PEC at this location; however, around the time period when the coal-tar sealant ban was implemented and a structural water control to capture stormwater runoff from a coal-tar sealed parking lot up gradient of the site was constructed, concentrations decreased to below the PEC at this site and have remained below the PEC. The combination of structural and regulatory best management practices appears to have reduced the PAH sources to Barton Creek, allowing concentrations in the creek to return to urban background levels.

Recommendations

While the ban seemed to limit sources to Austin creeks overall, there are several site locations where PAH concentrations are still above the Probable Effects Concentration. All sources of contamination at these sites are not known. While other PAH monitoring sites may be dropped from the sampling protocol, it is highly recommended that the following sites not only continue to be monitored but a new study should be designed and conducted to find sources of contamination:

1) Bull Creek at Loop 360
2) Buttermilk Creek at Little Walnut Creek
3) Carson Creek at US 183
4) Dry Creek North at Highland Pass
5) Eanes Creek at Camp Croft
6) East Bouldin Creek Downstream of W. Alpine Drive
7) East Bouldin Creek at Elizabeth Street
8) East Bouldin Creek at Post Oak
9) Harper's Branch Creek at Woodland Ave.
10) Little Walnut at Golden Meadow
11) Taylor Slough North at Pecos
12) Waller Creek at Pipe Upstream of 24th Street
13) Walnut Creek at Metric Blvd.

Most of the locations are highly urbanized but contain concentrations above what is accepted as urban background levels (Stout *et al* 2004). Further investigation will not only allow the City of Austin the opportunity to restore concentrations of PAH to background levels at these sites, but also provide insight on other probable sources of PAH contamination around Austin.

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